COMPLEXES OF MOLYBDENUM AND TUNGSTEN IN AQUEOUS SOLUTION.

BY

JAMES DUNCAN PATERSON McCALLUM

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Except the Lord build the house, they labour in vain that build it. Ps. 127, i.

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CONTENTS.

			Page No:
Abstract			1 - 11
Introduction:			1.
Experimental:	g.1.0	Single Ligand and Hetero-Complexes Involving Hydroxy-carboxylic acids.	21.
	g.2.0	Single Ligand and Hetero-Complexes Involving Sugars	42.
	g.3.0	Single Ligand and Hetero-Complexes Involving Poly-hydroxy Alcohols.....	60.
	g.4.0	Single Ligand and Hetero-Complexes Involving Hydroxylamine.....	68.
	g.5.0	Reactions of Complexes....	74.
Discussion:			79.
References:			111.

ABSTRACT.

A series of complexes has been prepared in aqueous solution between sodium molybdate (and sodium tungstate) and the organic ligands: D(+) tartaric, L(-)mandelic, oxalic, trans-aconitic and itaconic acids, the disodium salt of 1,2 dihydroxy-benzene - 3,5- disulphonic acid (tiron), D(+) mannose, D(-) ribose and L(-) sorbose, D-mannitol and D-sorbitol, and hydroxylamine. Two different types of complex were obtained, one with one ligand and the other with two ligands coordinated to the molybdate or tungstate ion.

All the complexes are strongly pH dependent in their formation, the pH range for complexing generally being between pH = 4.5 and 7.0, but with the polyhydroxy alcohols complexing can be obtained down to pH = 2.0. For pH values greater than 7.5 decomposition of the complexes into their constituents takes place, while for values of pH below 4.5 the molybdate and tungstate ion tend to polymerize. This latter fact suggests that the 2:1 metal: ligand ratio of polyhydroxy alcohol complexes may arise from the molybdate and tungstate ion being dimerized, since these complexes, as indicated above, at formed at a pH of 2.0. The methods used to determine the stoichiometry of the complexes were

optical density and optical rotation measurements.

The effects of light and heat on the complexes were observed by firstly irradiating the compounds with ultraviolet light and secondly refluxing them for several days. Although some of the complexes were unaffected (e.g. those of glycollic and citric acids) or were reduced to molybdenum blue (D-mannitol and D-sorbitol), others formed deep red coloured solutions which contained molybdenum (V) (D(+)tartaric acid, L(-) mandelic acid, D(+) mannose, D(-) ribose and L(-) sorbose), a redox mechanism operating between molybdate and the ligand. In the case of the mandelic acid complex an orange solid of composition $NaMoO_3.2H_2O$ was obtained, with benzaldehyde as the oxidation product of the mandelic acid.

The effects of various ions such as sulphate, carbonate, phosphate, nitrate and nitrite upon the refluxing solutions was also examined. It was found that sulphate, phosphate and carbonate ions inhibited the reduction in different ways. The effect of nitrate and nitrite ions depended on the nature of the ligand - sugar complexes were unaffected, the reduction of molybdate by mandelic acid was decreased and the tartrato complex was stabilized as the colourless molybdenum (VI) compound.

INTRODUCTION.

Molybdates and Tungstates in Aqueous Solution

In order to understand the equilibria operating in the systems studied it is necessary first of all to examine the chemistry of sodium molybdate and sodium tungstate in aqueous solution.

1. Sodium Molybdate

The state of the molybdate ion in aqueous solution is found to depend upon three factors : (a) the concentratio (b) the acidity and (c) the age of the solution, all three factors tending to lead to anionic aggregation. Despite the fact, however, that a wide range of methods, including dialysis and diffusion[1], conductiometric titration[2], pH titration[3], light scattering[4], cryoscopy[5], ion exchange[6] and U.V. spectra[7], have been used to study this polymerizatio effect there is still considerable disagreement as to the individual steps in the process.

Very broadly speaking there are three main species present in aqueous solution :

(a) the normal molybdate ion MoO_4^{2-}

(b) the paramolybdate ion, initially formulated as $[Mo_8O_{26}]^{4-}$ [8].

(c) the octamolybdate ion formulated as $[Mo_8O_{26}]^{4-}$ [8].

All investigators are agreed that the normal MoO_4^{2-} ion is present in all solutions of pH > 7.

Cooper and Salmon[10] using ion-exchange techniques suggest that the first stage of condensation takes place at pH = 6, there being three possible mechanisms of formation:

(i) $4MoO_4^{2-} + 6H^+ \rightleftharpoons Mo_4O_{13}^{2-} + 3H_2O$

(ii) $6MoO_4^{2-} + 9H^+ \rightleftharpoons H_3Mo_6O_{21}^{3-} + 3H_2O$ [11,12]

(iii) $8MoO_4^{2-} + 12H^+ \rightleftharpoons Mo_8O_{26}^{6-} + 6H_2O$ [13]

Mechanisms(ii) and (iii) they reject on the grounds that such structures require 5- co-ordinate oxygen atoms which is unlikely in solution whereas (i) does not. Their experiments show the ratio of metal ions to units of charge in the first polymer species to be equal to two, which led them to suggest that the paramolybdate ion can be represented as a flexible chain of four linked MoO_4^{2-} tetrahedra of formula $Mo_4O_{13}^{2-}$, thus confirming the work of Doucet[14] and Carpeni[15], Britton[16] and Cannon[17].

With regard to the second stage of polymerization Cooper and Salmon[10] suggest that with the metal ion/unit charge ratio of five there is formed the protonated species $H_3Mo_{10}O_{32}^{3-}$. This reaction is said to commence at pH = 4.5 but becomes faster below pH = 2.5. Addition of strong acid results in the decomposition of the second

polymerisation stage to form either molybdenyl cations[18] or molybdenum anions containing chloride as a ligand[19]. They found no evidence to support the existence of a heptamolybdate ion $[Mo_7O_{24}]^{6-}$.

Aveston, Anacker and Johnston[20], suggest that the graphical methods used to substantiate the tetrameric nature of the paramolybdate could equally well apply to any multiple of this unit e.g. $Mo_8O_{26}^{4-}$. Furthermore they point out that accurate information cannot be obtained from such methods regarding the possible protonation of the species because of the fact that the points of inflection on pH and conductiometric titration curves tend to broaden due to the co-existence of several molydate species at a given pH and total molydate concentration. Their own work using the ultracentrifuge indicates that the heptamer $Mo_7O_{24}^{6-}$ is the initial product of polymerisation and that this on further acidification yields the octamer $Mo_8O_{26}^{4-}$.

The existence of these two species, as opposed to the tetramer is supported by the molecular weight determinations of Glemser[21] et al. However, he suggests that it is the octamer which is the first polymerisation product, according to the equations:

$$8MoO_4^{2-} + 12H^+ \rightleftharpoons Mo_8O_{26}^{4-} + 6H_2O$$

and that from it there is possibly formed the heptamer as a result of the hydrolysis:

$$7Mo_8O_{26}^{4-} + 10H_2O \rightleftharpoons 8Mo_7O_{24}^{6-} + 12H^+$$

It would appear therefore that the equilibria present in solutions of molybdate are by no means established as yet, although the bulk of the evidence suggests that the MoO_4^{2-}, $Mo_8O_{26}^{4-}$ and $Mo_7O_{24}^{6-}$ ions are the species most commonly obtained.

2. Sodium Tungstate

A greater diversity of polymers is proposed for sodium tungstate in aqueous solution - at least eighteen different species being mentioned in the literature[22,23,24]. However, there would appear, once more, to be three main species present in solution, depending upon pH:

for pH > 9 the normal tungstate ion was represented as WO_4^{2-} [25,26,27].

pH 9-5 the paratungstate ion was represented as $[HW_6O_{21}]^{5-}$ [28].

pH < 5 the γ-metatungstate ion was represented as $[H_3W_6O_{21}]^{3-}$ [26].

The existence of the normal tungstate ion WO_4^{2-} in solutions above pH = 10 is well established, although some workers do maintain that it is present at pH = 8 [20].

The situation for the para and metatungstates is by no means so simple, since in both cases it has been claimed that there are in practice two para- and two meta-ions.

Jander and his co-workers[25,28,29] concluded from diffusion studies that the dominant species in solution between pH = 8 and 6 is $[HW_6O_{21}]^{5-}$ as formed in the reactions:

$$6WO_4^{2-} + 7H^+ \rightleftharpoons [HW_6O_{21}]^{5-} + 3H_2O$$

However, Souchay[26] claimed from his cryoscopic, potentiometric and polarographic experiments that there are two paratungstates (A and B) which posses the same formula but differing characteristics. Thus, for example, paratungstate A according to Souchay yields on acidification 'γ-metatungstate' $[H_2W_6O_{21}]^{6-}$ whereas paratungstate B does not react with H^+. Further work by Jander and Krueke[30] confirmed the existence of the two species and resulted in the additional suggestion that there were also two γ-metatungstates (A and B) both of formula $[H_2W_6O_{21}]^{6-}$. Sasaki[32] from equilibrium studies in 3M sodium perchlorate

was able to confirm Jander's original surmise as to the formula of the paratungstates as $[HW_6O_{21}]^{5-}$.

Aveston[32], however, using ultracentrifugation, acidity measurements and Raman spectra and Craig and Tyree[33] using light scattering techniques suggest that in freshly prepared solutions of sodium paratungstate, $(Na_{10}W_{12}O_{41})28H_2O$, the main species is the ion $[W_{12}O_{42}]^{10-}$ and that this hydrolyses slowly to a mixture of $[W_{12}O_{41}]^{10-}$ and $[HW_6O_{21}]^{5-}$. They find no evidence in support of the ion $[H_3W_6O_{21}]^{3-}$ proposed by Souchay[26] and Sasaki[34], but in accordance with the work of Jander[30] suggest that at higher acidity the $[W_{12}O_{39}]^{6-}$ ion is formed.

The most recent suggestions regarding the paratungstate ion come from Glemser and Holtse [35] who maintain on the basis of molecular weight studies that the paratungstate A should be formulated as $[W_6O_{17}(OH)_7]^{5-}$ according to the equation:

$$7H^+ + 6WO_4^{2-} \rightleftharpoons [W_6O_{17}(OH)_7]^{5-}$$

and that this in turn gives rise to the paratungstate B $[W_{12}O_{36}(OH)_{10}]^{10-}$:

$$2[W_6O_{17}(OH)_7]^{5-} \rightleftharpoons [W_{12}O_{36}(OH)_{10}]^{10-}.$$

This latter formula is in accord with the Xray work of Schwarzmann[36]. Glemser and Holtze[35] indicate that it is possible to distinguish between freshly prepared solutions of paratungstate A and B by means of a characteristic shoulder in the U.V. spectrum. They point out that the spectra of the solutions change with time, showing an increasing similarity until finally they become the spectra of metatungstates.

An alternative suggestion is put forward by Lipscomb[37], on the basis of Xray work, that the paratungstate B should be represented as $[W_{12}O_{40}(OH)_2]^{10-}$ whereupon the equilibrium between A and B would become:

$$2[W_6O_{20}(OH)]^{5-} \rightleftharpoons [W_{12}O_{40}(OH)_2]^{10-}$$

With regard to metatungstates Glemser and Holtze express doubts regarding the reliability of Souchay's methods of arriving at the formula $[H_3W_6O_{21}]^{3-}$ which has considered to be formed:

$$9H^+ + 6WO_4^{2-} \rightleftharpoons [H_3W_6O_{21}]^{3-} + 3H_2O.$$

Using the ultracentrifuge method, with potassium -12-silicotungstate as a control, the molecular weight measurements tend to indicate the formula $[W_{24}O_{72}(OH)_{12}]^{12-}$ for the metatungstate ion - this being the highest aggregation yet

suggested for a polymerized molybdate ion.

The above reactions indicate the nature of the polymerisation equilibria operating in solutions of molybdate and tungstate ion.

Complexes of Molybdate and Tungstate Containing One Type of Organic Ligand.

Normal molybdate and tungstate ions form complexes in aqueous solution with a wide range of organic molecules containing hydroxy groups e.g. (a) hydroxy-carboxylic acids[39-53], (b) phenols[54-61] and substituted phenols[61-65] (c) polyhydroxy compounds[66-79], (d) sugars[80-84], (e) sulphonic acids[85,86], (f) dioximes[87], and O-dihydroxy-coumarins[88], the bulk of the work having been done on the first four classes of ligand.

(a) Complexes with Hydroxy-Carboxylic Acids. Complexes have been claimed with tartaric[39-44] oxalic[45-46], mandelic[47,48] gluconic[49,50], lactic[51], malonic[52], citric[41], malic[42], glycollic[47] and succinic acids[42]. One of the earliest studies of tartaric acid was made by Theoderesco[39] who, from a comparison of the Raman spectra of tartaric acid, sodium tungstate and sodium tartratotungstate concluded that the complex probably existed as $Na_2[C_4H_4O_6.WO_3]$.

Viscosity and f.p. depression measurements by Prasad and Krishnaiah[43] and equilibrium constant studies by Yatsimirski[53] confirmed the 1:1 ratio of metal to ligand. More commonly, however, polarimetric, conductiometric and potentiometric measurements are employed[43,44,46]. Baillie and Brown[42] have suggested that as the pH of the tartrato-system is increased the following sequence of operations is obtained:

$$WO_4^{2-} + C_4H_6O_6 \rightleftharpoons [WO_4 \cdot C_4H_5O_6]^{2-}$$

$$\downarrow\uparrow$$

$$[WO_4 \cdot C_4H_5O_6]^{3-} + H^+$$

$$\downarrow\uparrow$$

$$WO_4^{2-} + C_4H_4O_6^{2-} \rightleftharpoons [WO_4 \cdot C_4H_4O_6]^{4-} + H^+$$

At pH = 4.2 the $[WO_4 \cdot C_4H_6O_6]^{2-}$ form exists almost exclusively; at pH = 7 the $[WO_4 \cdot C_4H_5O_6]^{3-}$ form and at pH = 8.2 the $[WO_4 \cdot C_4H_4O_6]^{4-}$ ion. The tetrabasic complex is stable up to a pH = 11, above which decomposition into sodium tartrate and sodium tungstate occurs. The tendency for the tungstate ion to polymerise is inhibited down to pH = 4.2, but below this value there arises increasing competition between the tendency to complex formation and polymerization.

It has been suggested[42] that the oxygens of the carboxylic group are involved in the bonding with the

central tungstate or molybdate ion. When therefore there is only one such group present in the molecule 2:1 ligand-metal complexes are formed. 2:1 complexes are also obtained with aromatic α-hydroxy carboxylic acids such as mandelic acid.

In one or two instances it has been found that the ratio of ligand to metal alters with differing environmental circumstances. Thus Spence and Kallos[49] have found that at pH = 2 the ratio of molybdenum(VI) to gluconic acid is 2:1 but that this alters with increasing pH until a 1:1 ratio is obtained. This alteration, they suggest, may be due to changes in the state of polymerization of the molybdate with pH.

Finally, in the case of the oxalato complex - although the 1:1 complex is the most stable the suggestion has been made[45] that the tungstate forms a $WO_4^{2-}:C_2O_4^{2-}$ complex with the ratio 1:6 while the corresponding molybdate has a 1:4 ratio. At low values of pH Vorontsova and Tananaev[46] claim, on the basis of conductiometric and potentiometric measurements, the existence of the complex $Na_4W_2O_5(C_2O_4)_3$.

(b). Complexes with Phenols and Substituted Phenols: As with mandelic acid so it is possible to form a series of 1:2 metal-ligand complexes with phenol-type molecules such as catechol[54-58] pyrogallol[58,60] and tiron[61], all of the complexes being strongly coloured (red).

In the case of catechol it is claimed[55] that although the 1:2 complex is the most stable in solution between pH 4 and 7 there also exist 1:1, 1:3 and 1:4 [58] complexes, the 1:4 complex being formed in the presence of concentrated sulphuric acid. From infrared studies[55] carried out on the 1:1 complex precipitated from solution by the addition of lead or barium salts Brown has shown that the complexing agent is probably the complete catechol molecule and that there is no elimination of water or of hydroxyl ions as a result of complex formation.

With pyrogallol three ratios are obtained depending upon pH: a 1:2 molybdenum:ligand complex between pH = 6 and 8, a 1:1 at pH = 3.5[60] and a 2:3 complex under strongly acid conditions[59]. Tiron, on the other hand, only forms two complexes: a 1:1 at pH = 2.8 and 1:2 at at pH $>$ 6.

Buchwald and Richardson[54] have suggested that at low

pH values the composition of the complex is a function of the substituent groups other than the hydroxyl groups involved in the bonding to the molybdenum or tungsten. This statement, however, would appear to require some qualification - for the following reasons. Firstly, their suggestion is based on studies of gallic acid and of 3,4 dihydroxy-benzoic acid - but in both these cases the oxygens of the carboxylic groups could be envolved in the bonding - thus altering the metal:ligand ratio. Secondly work performed on acetopyro-[62], 4-chloro[64] and 4-methyl catechol[65] indicates that a 1:2 metal ligand complex is obtained in each case and that only a small amount of the 1:1 4-chloro-catechol complex is obtained at low pH values. It is much more probable that the increase in the ratio of molybdenum to ligand is due to the polymerization of the molybdate or tungstate ion. Such a suggestion would appear to be confirmed by Buchwald and Richardson's own postulation of the formation of a 1:2 catechol-molybdate complex at pH $\geq$ 2 and by Schnaiderman and Khrustalev's[59] 1:4 complex present in concentrated sulphuric acid solution.

(c) Complexes with Polyhydroxy Molecules: Although it has long been known[61-76] that complexes can be formed

between molybdate and tungstate and polyhydroxy compounds it is only in very recent years that this field has begun to be developed. By using paper - electrophoretic methods in addition to polarimetric measurements Bourne, Hudson and Weigel[77] and Angus[78,79] have shown that complexes can be obtained with tetritols, pentitols and their derivatives, and hexitols and their derivatives. The fact that, although maximum complex formation takes place at about pH = 2, there is some complexing over the whole range pH = 1-8 means that measurements may be made at about pH = 5.0 i.e. at a pH which allows both immediate complex formation and a fair degree of ionization to take place.

The length of the carbon chain is one of the factors governing the ratio of components. Thus, with tetritols such as erythritol a 1:1 ratio is obtained. With more than four carbons in the chain the ratio determining factors becomes the proximity of the hydroxyl groups to each other and their steric arrangement on the carbon chain. From a comparative study of polyhydric alcohols and their corresponding deoxy derivatives Bourne et al[77] and Angus[78,79] have found that it is necessary for the complexing molecule to possess a ratio of three adjacent hydroxyl groups per molybdenum involved in the bonding.

They make the additional suggestion that the complexing species is not the simple MoO_4^{2-} (or WO_4^{2-}) ion but the dimeric form $Mo_2O_7^{2-}$ (or $W_2O_7^{2-}$). The main factor in support of this polymerization is the low value of pH (2.0) at which maximum complexing is said to take place.

As yet no structural studies have been performed to uphold these suggestions and the structures proposed by Angus are based solely on the comparative study of a large number of deoxy compounds and their parent polyhydric alcohols.

(d) Complex with Sugars: Once more it is only in recent years[30-34] that a critical study has been made of the ability of sugars to complex with molybdate and tungstate. Bourne, Hudson and Weigel[32], using paper ionophoresis methods found that pyranose sugars (in the chair-form) possessing three hydroxyl groups in a cis-cis-1(ax), 2 (eq), 3(ax) arrangement formed 1:1 complexes with molybdate. Spence and Kiang[34] verified these results, finding from polarimetric studies that at pH about 5.0 there was a large change in the value of optical rotation of sugars dissolved in molybdate solution - this change being indicative of complex formation. Both Bourne and Spence suggest that all three hydroxyl groups are necessary for

complexing to take place since the replacement of a hydroxyl group by a hydrogen atom destroys the ability to complex. However, in view of the fact that Angus, Bourne, Searle and Weigel[84] have shown that at least one of the hydroxyl groups can be replaced by a primary amino group it would appear that the oxygen of the third hydroxyl group cannot be directly bonded to the molybdenum or tungsten atom. Indeed for it to be so bonded would require the metallic atom to be seven-coordinate, since so far, there has been no evidence to suggest that the coordination number is reduced by the dimerization of the molybdate or tungstate species. Likewise the fact that maximum complexing occurs in the region of pH = 5.0 militates against any such polymerization. Perhaps the explanation lies in the fact that the hydroxyl group or amino group are involved in some form of hydrogen bonding necessary to the stabilization of the complex.

(c) Complexes With Other Oxygen-bearing Ligands: The existence has been claimed of 1:1 complexes between sulphonic acids,[85,86] dioximes[87] and dihydroxy coumarins[88] and molybdate in which once more the oxygens of the molecules are involved in the bonding to the central metallic ion. In the

case of amino acid complexes Spence and Chang[89] record a cysteine complex in which the cysteine:metal ratio varies from 3:1 to 1:1 depending upon the concentration of the reagents. They suggest, on the basis of spectrophotometric studies that the bonding involves both the ionised mercapto and carboxyl groups.

The Possibility of the Existence of a Complex Containing Two Different Ligands Simultaneously Attached to the Central Molybdate or Tungstate Ion.

From the above it has been shown that the metal:ligand ratio can vary from 2:1 to 1:1 to 1:2 etc. This tends to suggest that a ligand may be introduced into a complex to form a 1:1:1 complex in which the two ligands attached to the central molybdate or tungstate ion are different. Similarly the 2:1 metal-alcohol ratio of certain of the polyhydroxy complexes suggests that it may be possible for further complex formation to take place with a second ligand.

The Reactions of Molybdate and Tungstate Complexes.

The reactions of both tungstates and molybdates and of their complexes are of profound interest because of the many applications in the fields of biology and analysis.

Applications in analysis involve the use of the physical

properties of the complexes such as colour. Thus Buchwald[90] has used the polyhydric alcohol complexes for the colorometric determination of molybdenum, while Halmekoski[91] uses the catechol complex in the spectrophotometric determination of mixtures of molybdenum and tungsten.

In the field of organic chemistry chromic acid is widely used for the oxidative cleavage of double bonds in highly substituted ethylenic compounds. Although the exact nature of the mechanism of the process is not known it has been suggested[92] that there must exist aqueous equilibria which involve species such as H_2CrO_4, $H_2Cr_2O_7$ and $(HCrO_4)^-$. The similarity of these species to those of molybdenum raises the question of whether molybdic acid can be used to these ends.

It is, however, in the field of biology that molybdenum comes into its own. Both plants and bacteria are found to require a certain level of molybdenum present in the soil or in the nutrient substrate before they are able to fix atmospheric nitrogen. Soils deficient in this necessary trace element can be rendered productive by the carefully controlled addition of sodium or ammonium molybdate. It was found, for example, that the inhibition of nitrogen fixation in Clostridium pasteurianum[93] caused by the presence of

trichloromethyl sulphenyl benzoate can be overcome by the addition of sodium molybdate. Again, when fumaric or malic acid is used to reactivate the enzymes which catalyse the disappearance of hydroxylamine in Escherichia coli[94] the process was found to be stimulated by the presence of molybdates.

For some time there was uncertainty as to whether the molybdenum species merely acted as catalysts and only formed a transient complex in some intermediate state in the reactions or whether the molybdenum was a constituent of the enzymes themselves. Then it was discovered that sodium tungstate[95] competed with molybdenum in the formation of nitrate reductase in Neurospora crassa . When the concentration of sodium tungstate was 10^4 times greater than the molybdate present the result was inhibition of 70% of the effect of molybdenum on the enzyme. The reason for this inhibition may well lie in the preferential formation of a tungstate complex species in place of molybdate, and that the molybdenum is in fact part of the enzyme molecule. This was indeed found to be the case. Redert and Westerfield[96] on studying the deposition and maintenance of normal levels of xanthine oxidase in the intestines of rats found that all of the

biological activity depended on the presence of molybdenum. Machler, Mahler and Green[97] produced the additional information that xanthine oxidase require the presence of molybdenum for enzymic activity with cytochrome C, although it was not necessary for activity with dyes or oxygen. Inorganic phosphates also appear to be essential for activity. Similar work with hydrogenase[98] revealed that the activity of the purified enzyme could only be restored by the addition of both FAD (flavinadenine dinucleotide) and molybdenum.

The most significant advance was made by Nicholas and Nason[99] who claimed, on the basis of dialysis experiments, that molybdenum is the metal constituent of nitrate reductase in Neurospora crassa. They found that molybdenum deficient nutrient media resulted in a decrease in nitrate reductase produced, which was quite different from the loss of enzymic activity produced by the removal by cyanide dialysis of the molybdenum from the intact enzyme. In the first case the addition of molybdenum to cell-free extracts produced from molybdenum deficient substrates did not result in the development of enzymic acitivity. But in the second instance the inactivated enzyme could be almost completely restored by the direct addition of the metal to the protein. Furthermore,

of all the micronutrient deficiencies only molybdenum deficiency resulted in a decrease in nitrate reductase activity. These facts indicate that molybdenum is a constituent of the enzyme itself. As yet nothing is known of the exact function of the molybdenum in the enzyme but presumably it is involved in some form of complex formation analogous to the anionic complexes described above.

One further, rather curious fact is that rats[100] are able to develop the ability to detect the presence of molybdenum in their diet and make use of this in rejecting diets containing toxic levels of molybdenum (the toxicity being due to attack of the long bone structures) the suggestion being that this sensory factor is due to the interaction of the molybdate with the dietary constituents.

Since it has been shown that the reactions of molybdate complexes are important in nature it was decided to examine some of these reactions with simple ligands in some of the complexes prepared.

EXPERIMENTAL: SECTION ONE:-

Single Ligand and Hetero Complexes With Molybdate and Tungstate Ions Involving Hydroxy-carboxylic Acids and Dihydroxy-phenols.

The methods used to investigate the nature of the complexes formed, made use of the variation of the physical properties of a ligand on forming a complex - in particular, the variations in optical density and optical rotation. These variations were examined over a limited pH range (pH = 2 to 10) since below pH = 2 polymerization of the molybdate and tungstate ions occurred while above pH = 10 alkaline hydrolysis occurred. After the adjustment of pH and dilution the samples were left to equilibrate for about 2 hours and the pH again measured. The stoichiometry of the complexes was investigated by means of Job's 'Continuous Variations Method', the plots being constructed at the pH where maximum complexing occurred. The existence of the hetero complexes (i.e. complexes having two differing ligands attached to the metallic ion or ions) was confirmed by measurements of different physical properties, each characteristic of one of the ligands.

Notes on Apparatus: The instruments used to measure pH values were the Pye 'Dynacap' pH Meter, and the Marconi type TF 1093 and TF 511D models, all of which employed a dip-type calomel electrode - glass electrode cell. Conductivities were obtained using the Wayne-Kerr Universal Bridge (B 221). Either

the Unicam Spectrophotometer S.P. 600 or the Hilger Uvispek Photoelectric Spectrophotometer H 700.307 were used to measure optical densities while optical rotation values were obtained from the Hilger Standard Polarimeter (Mark III) employing a sodium lamp.

gl.1. Complexes with D(+) Tartaric Acid and with the Di-sodium Salt of 1,2-Dihydroxy - Benzene-3,5- Disulphonic Acid. ('Tiron').

(a) Variation of Optical Density with pH: Measurements here were concerned with the effects of the presence of tartaric acid on the optical density of the tiron-molybdate complex. Accordingly 100 ml. of 0.002M sodium molybdate-tiron complex were prepared by mixing 20 ml. of 0.01M sodium molybdate with 40 ml. of 0.01M tiron and making the resultant solution up to 100 ml. 10 ml. samples were diluted to approximately 50 ml. each, the pH of the samples adjusted over the range 2 to 10 by the addition of dilute hydrochloric acid and sodium hydroxid and finally the solutions made up to 50 ml. each. After allowing the solutions to equilibrate for two hours the pH of the samples was again measured. Spectroscopic examination of the samples was carried out at 425 mμ and the resultant valu of optical density plotted against pH (graph 1a).

Equal volumes of sodium molybdate and D(+) tartaric acid (20 ml. 0.01M) were mixed with 40 ml. 0.01M tiron and the whole diluted to 100 ml. The pH and concentration of 10 ml. samples were adjusted as above and again the optical density measured at 425 mμ and plotted against pH (graph 1b).

In the case of the tungstate analogue the less intense colouration of the solutions (yellow as compared with orange-red) enabled higher concentrations to be used. Here 5 ml. samples of 0.04 M sodium tungstate-tiron and sodium tungstate-tiron-D(+)tartaric acid complex solutions were diluted to 50 ml. with the appropriate pH adjustments and their optical density measured at 425 mμ and plotted against pH (graphs 1c and 1d respectively).

The stability of the hetero complex was examined by treating samples containing equimolar quantities (10 ml. 0.2M) of sodium tungstate and D(+) tartaric acid with saturated (6M) tiron solution in increasing quantities until a 40 - fold excess of tiron was present in the final sample. After pH adjustment to 4.5 each sample was diluted to 50 ml. and the optical rotations measured. For optical density values at 425 mμ ten-fold diluted samples were used. It was found that after the addition of one equivalent of tiron a steady value of

optical rotation and of optical density was attained.

(b) Variation of Optical Rotation with pH: By observing possible variations in the value of optical rotation of tartaric acid the effect of introducing tiron into the tartrato complex could be noted. Using a similar method to that described for the optical density measurements the pH of a number of samples of 0.005M tartrato-molybdate and of tartrato-molybdate plus tiron were varied between pH = 2 and 10 and the resultant values of optical rotation measured (using a 20 cm. tube and sodium D light) and plotted against pH (graphs 2a and b). The metal ion concentration in the tungstate systems was 0.04M (graphs 2c and d) Graph 2c indicates that the optical rotation of D(+) tartaric acid (0.04M) alone is scarcely affected by altering pH.

(c) The Stoichiometry of the Complex - The Job's Plot: A method for determining the stoichiometry of complexes formed in solution by the interaction of two components was devised by Job[102]. In this method the variation produced in some physical characteristic of one of the reactants is observed as the mole fraction of this reactant is increased. For the purposes of this work the physical characteristic chosen was

optical density measured at a set value of pH and wavelength (425 mμ). Accordingly portions of 0.001M tartrato-molybdate were mixed with 0.001M tiron in the proportions 1 ml. tartrato-molybdate: 9 ml. tiron, proceeding by 1 ml. stages to the proportion 9 ml. tartrato-molybdate: 1 ml. tiron. The samples were each made up to 50 ml. after pH adjustment to 4.5, and the values of optical density measured at 425 mμ. (graph 3a). 0.01M reagents were used for the tungstate complex (graph 3b). Both maxima occur at 0.5, i.e. 1:1:1: complexes were foxmed.

g1.2. Complexes with L(-) Mandelic Acid and with Tiron

(a) Variation of Optical Density with pH: Unless otherwise stated the technique used in these and in all other experiments was the same as that for the tartrato system described above, all samples being made up to 50 ml. each after the appropriate pH adjustment and the values of optical density measured.

The quantities of materials mixed in nine 50 ml. samples of pH 2-10 were 0.5M sodium molybdate, 1 ml. 0.2M L(-) mandelic acid (mandelic acid forming a 1:2 molybdate: acid complex) and 1 ml. 0.2M tiron. Nine samples were prepared containing 5 ml. 0.2M sodium tungstate mixed with equimolar quantities of L(-) mandelic acid and tiron (10 ml. 0.2M) each sample being made up to 50 ml. (A), after pH adjustment. 5ml. samples were each diluted with 10 ml. of water and the optical densities measured

at 425 mμ. (graphs 1e and f).

(b) Variation of Optical Rotation with pH: Unfortunately the deep red colour of the solutions did not permit optical rotation measurements to be made on the instrument available. Neither by altering the wavelength of the polarimeter lamp (from sodium D to mercury) nor by dilution of samples could this difficulty be overcome, since in the latter case the optical rotation had reached zero value by the time it was possible to observe the split-image of the polarimeter. The orange colour of the hetero-tungstate solutions enabled optical rotation measurements to be taken, using the samples diluted to strength (A) mentioned above and the results are plotted on graphs 4a, b and c.

(c) Stoichiometry of the Complex - The Job Plot: Since, in this instance, both ligands form 1:2 complexes there will actually be excess mandelic acid present in the samples. This in no wise affects the validity of the results since neither mandelic acid nor the mandelo complex is absorbing at the wavelength used. 0.01M tiron was introduced into samples containing the 2:1 mandelo-molybdate complex (samples being taken from 100 ml. of solution of the complex prepared by

mixing 5 ml 0.2M sodium molybdate with 10 ml 0.2M L(-) mandelic acid made up to volume). The portions taken were 1 to 9 ml mandelo complex mixed with 9 to 1 ml respectively of tiron solution, all samples being made up to 50 ml after pH adjustment to 4.5. The same strength of solutions was used for the tungstate complex (graphs 3c and d). Again the maxima were found at 0.5 where the ratio of components is 1:1:1.

§ 1.3 Complexes with Both Oxalic Acid and D(+) Tartaric Acid.

(a) Plot of Optical Rotation Against Mole Equivalent of Added Oxalic Acid: Here the changes in optical rotation of the tartaric acid provided the most convenient method of following the interaction of oxalic acid with the tartrato-complex, the same concentrations being used for both molybdate and tungstate complexes. Nine samples were prepared containing equimolar sodium molybdate (or tungstate) and D(+) tartaric acid (10 ml 0.2M) and to them was added molar oxalic acid in the quantities: 0.5 ml, 1 ml, 1.5 ml, 2 ml, 3 ml, 4 ml, 5 ml, 10 ml, and 15 ml, the solutions each being made up to 50 ml and the pH adjusted to 4.2. The values of optical rotation were measured and plots prepared of optical rotation against equivalents of molar oxalic acid added (graphs 5a and b).

(b) Stoichiometxy - The Corrected Job Plot: Spence and Kiang[83] adapted the original Job's 'Method of Continuous Variations' for those systems in which the excess of the reacting ligand possessed a significant optical rotation of its own. By subtracting the values of optical rotation due to excess ligand (in this case tartaric acid) from the values for the solutions containing the hetero complex plus this excess acid, the optical rotation for the hetero complex alone is obtained and plotted against mole fraction in the normal manner. To samples containing 2 to 18 ml of 0.1M oxalato tungstate (or molybdate) was added 0.1M D(+) tartaric acid in the quantities 18 ml to 2 ml. The samples were made up to 50 ml each after pH adjustment to 4.0 and the values of optical rotation obtained. Four additional samples were prepared containing 16, 12, 8 and 4 ml 0.1M D(+)tartaric acid and the pH values, final volumes adjusted and determined as before. By subtraction of the values of optical rotation of these compensating solutions from the initial samples containing the tartrato-oxalato- tungstate (and molybdate) complex and excess uncomplexed tartaric acid the values of optical rotation for the hetero complex alone was obtained. The results were plotted on graph 3e, sim-

ilar results being obtained for the molybdate complex, the maxima occurring at the molar ratio of 0.5.

g 1.4 Complexes With Trans-aconitic Acid and The Corresponding Hetero Complexes With Tiron.

(i) Conductivity Plot for The Complex With Trans-aconitic Acid: Use was made of this method because of the fact that there is no difference between the U.V. spectra of the complexes and the ligand. A 100 ml sample of 0.001M sodium molybdate was titrated against 0.04M trans-aconitic acid (graph 6a) to obtain a minimum at 2.00 ml of added acid. For a 1:1 complex the equivalence point for the addition of the acid (tri-basic) is 2.50 ml.

(ii) Hetero Complexes With Trans-aconitic acid and With Tiron.

(a) Variation of Optical Density With pH: 100 ml of the hetero solution was prepared by mixing 1 ml each of 0.2M sodium molybdate and trans-aconitic acid with 2 ml of 0.2M tiron. 10 ml samples were diluted five-fold after pH adjustment and the resultant optical densities plotted against pH (graph 7a) and compared with those for the tiron complex alone (graph 7b).

For the tungstate complex 20 ml 0.2M tiron was mixed with

equimolar quantities of sodium tungstate and trans-aconitic acid (10 ml 0.2M) and the whole made up to 50ml. Ten-fold dilution of samples after pH adjustment produced the solutions used for the optical density measurements at 425mμ (graphs 7c and d).

(b) Stoichiometry - The Job Plot: 9ml to 1 ml samples of 0.01M tiron were respectively mixed with samples containing 1 ml to 9 ml of 0.01M trans-aconitic acid-molybdate complex (prepared by mixing 5 ml of each of 0.2M sodium molybdate and trans-aconitic acid and making up to 100 ml) and each sample made up to 50 ml after pH adjustment to 4.5. Values of the resultant optical densities at 425 mμ were plotted against mole fractions of trans-aconitic acid complex (graph 8a). 0.1M reagents were used in the case of the tungstate complex (with the same ratio 1 ml .... 9 ml, 9 ml .... 1 ml) (graph 8b). However, whereas the maximum for the molybdate complex is at 0.5 that for the tungstate is at 0.33.

g 1.5 Complexes With Itaconic Acid and the Corresponding Hetero Complexes With Tiron.

(i) Conductivity Plot for the Complex With Itaconic Acid: As with aconitic acid so with itaconic acid the conductivity plot

was used to examine the possibility of complex formation. 0.04M acid was titrated against a 100 ml sample of 0.001M sodium molybdate to give the resultant graph (6b), the minimum being found to occur at 3.50 ml added acid. Again, the theoretical equivalence point for a 1:1 complex is 2.50 ml.

(ii) Hetero Complexes With Itaconic Acid and With Tiron.

(a) Variation of Optical Density with pH: 2 ml of each of 0.2M sodium molybdate and itaconic acid were mixed, 4 ml 0.2M tiron added, and the whole made up to 200 ml. 20 ml samples were diluted to 50 ml after the appropriate pH adjustment and the optical densities measured and compared with those for the tiron complex alone (graphs 9a and b respectively).

100 ml of tungstate complex was prepared by mixing 40 ml 0.2M tiron with equimolar quantities of sodium tungstate and itaconic acid (20 ml 0.2M). Following pH adjustment, five-fold dilution of samples provided the solutions for optical density measurements. (graphs 9c and d)

(b) Stoichiometry - The Job Plot: Equal quantities of sodium molybdate and itaconic acid (5 ml 0.2M) were mixed and the whole made up to 100 ml. To samples containing respectively 1 ml to 9 ml of this solution were added samples containing

9 ml to 1 ml of 0.01M tiron. The resultant solutions were made up to 50 ml each after pH adjustment to 4.5 and the optical densities measured and plotted against mole fraction of the itaconic acid complex (graph 8c). Where the tungstate complex was concerned 0.1M reagents were used in the same proportions to obtain graph 8d. Again it was found that the peak for the molybdate complex lay at 0.5 while that for the tungstate lay at 0.33.

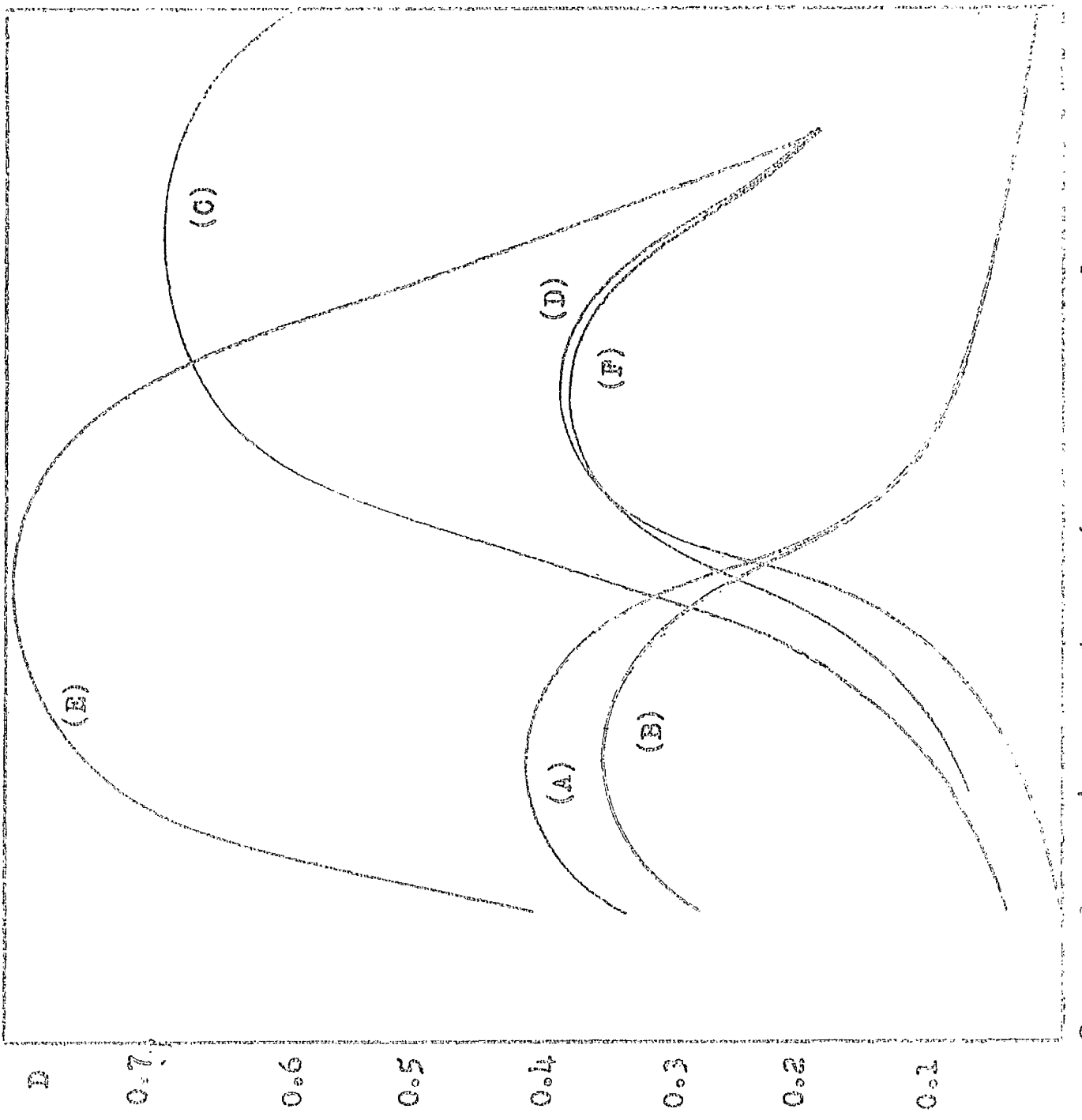


FIG. 1. - Optical Density at 425 mμ plotted against pH for:
(A) 4 x 10^{-4}M sodium molybdate and 8 x 10^{-4}M tiron.
(B) 4 x 10^{-4}M sodium molybdate and D(+) tartaric acid, and 8 x 10^{-4}M tiron.
(C) 4 x 10^{-3}M sodium tungstate and 8 x 10^{-3}M tiron.
(D) 4 x 10^{-3}M sodium tungstate and D(+) tartaric acid, and 8 x 10^{-3}M tiron
(E) 2 x 10^{-3}M sodium molybdate, 4 x 10^{-3}M L(-) mandelic acid and 4 x 10^{-3}M tiron,
(F) 2 x 10^{-2}M sodium tungstate, 4 x 10^{-2}M L(-)Mandelic acid and 4 x 10^{-2}M tiron.

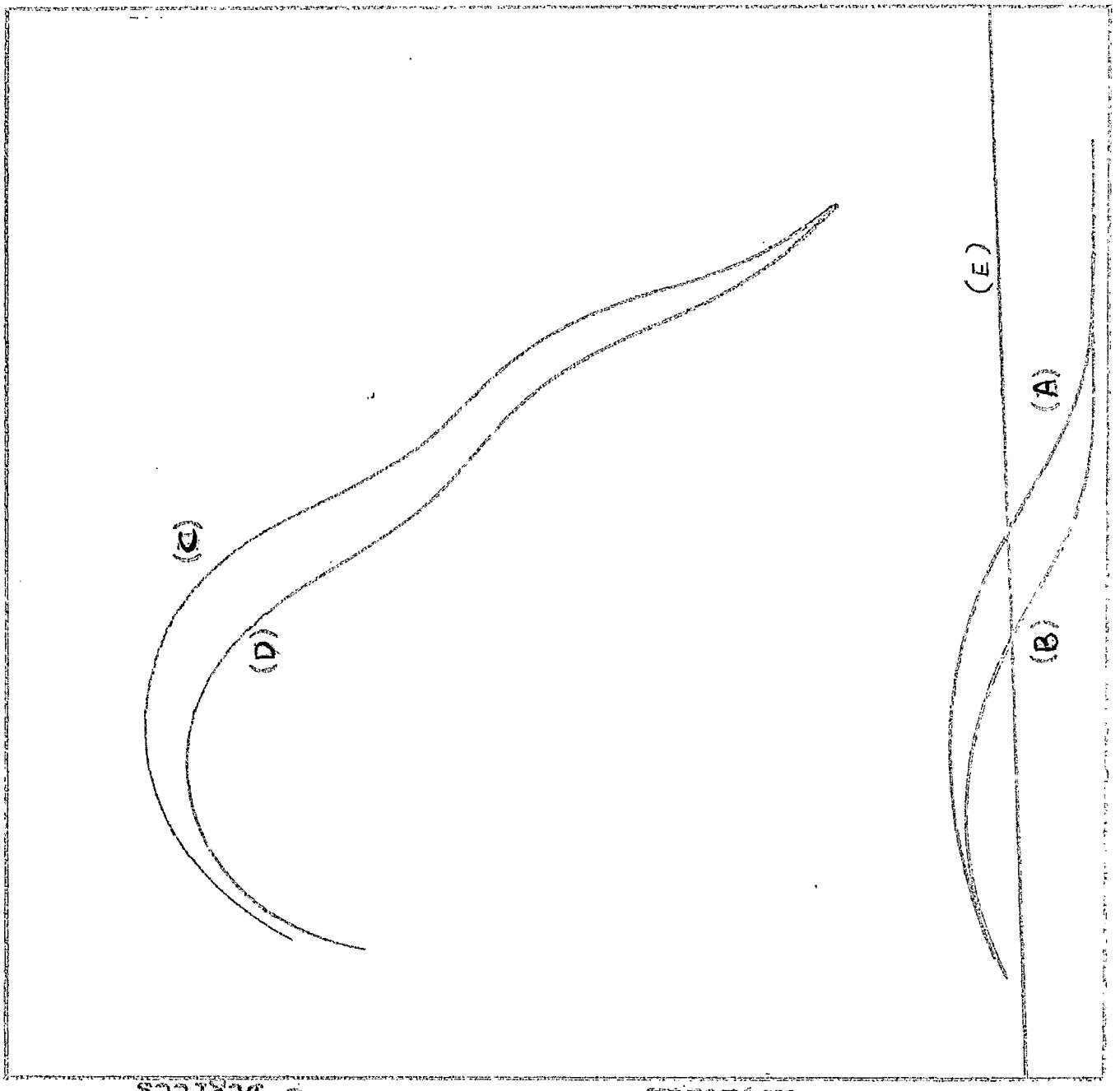


FIG. 2. - Optical Rotation plotted against pH for:

(A) 5 x 10^{-3}M sodium molybdate and D(+) Tartaric acid:

(B) 5 x 10^{-3}M sodium molybdate and D(+) Tartaric acid, and 1 x 10^{-2}M tiron.

(C) 4 x 10^{-2}M sodium Tungstate and D(+) Tartaric acid:

(D) 4 x 10^{-2}M sodium tungstate and D(+) Tartaric acid, and 8 x 10^{-2}M Tiron.

(E) 4 x 10^{-2}M D(+) Tartaric acid.

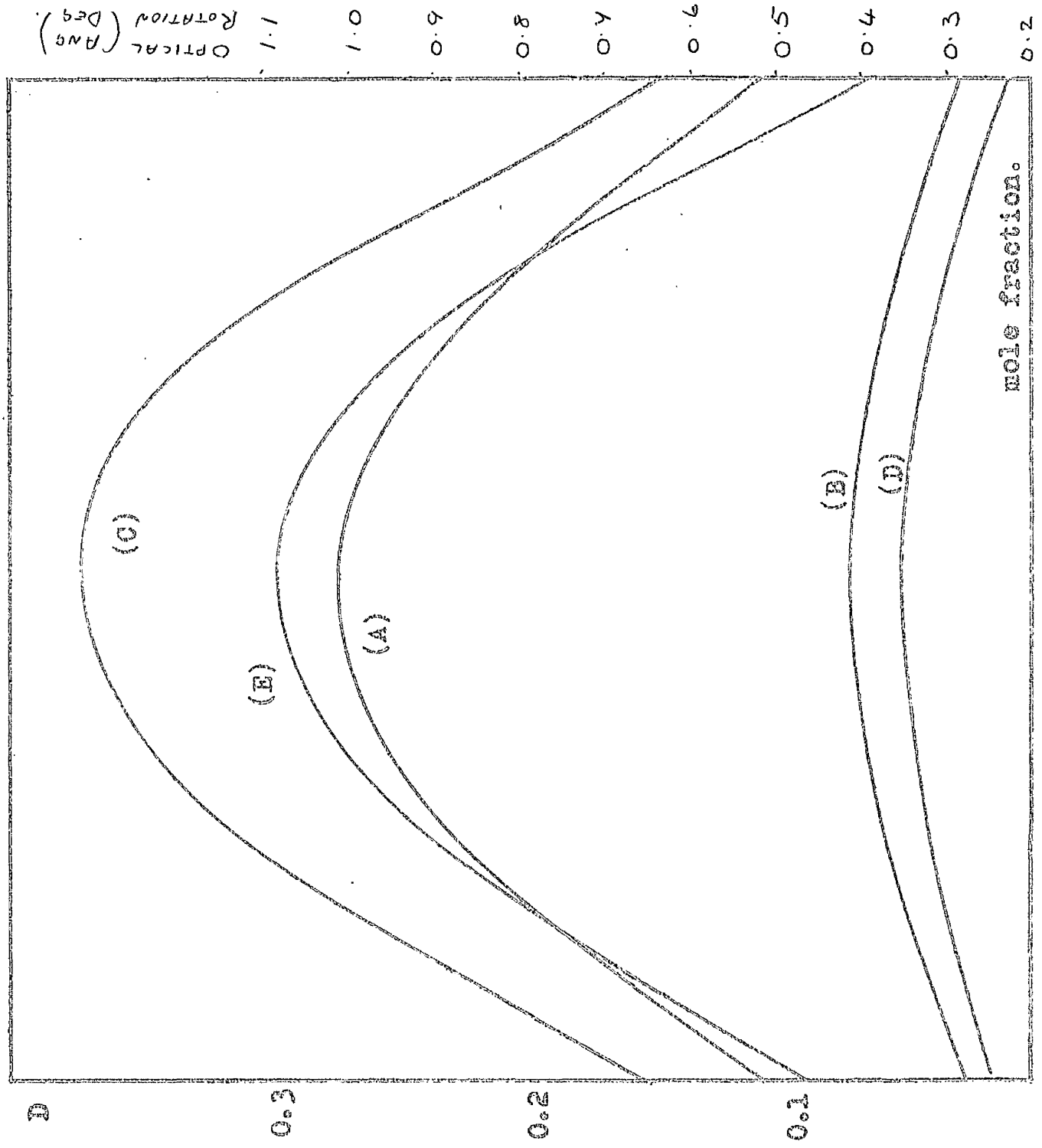


FIG. 3. - Optical density at 425 mu plotted against molar fraction of acid-molybdate complex at pH 4.5:

(A) 1 x 10^{-3}M D(+) tartrato-molybdate and 1 x 10^{-3}M Tiron

(B) 1 x 10^{-2}M D(+) tartrato-tungstate and 1 x 10^{-2}M Tiron

(C) 1 x 10^{-2}M L(-) mandelo-molybdate and 1 x 10^{-2}M Tiron

(D) 1 x 10^{-2}M L(-) mandelo-tungstate and 1 x 10^{-2}M Tiron

(E) 1 x 10^{-1}M oxalato-tungstate and 1 x 10^{-1}M D(+) tartaric acid. (OPTICAL ROTATION)

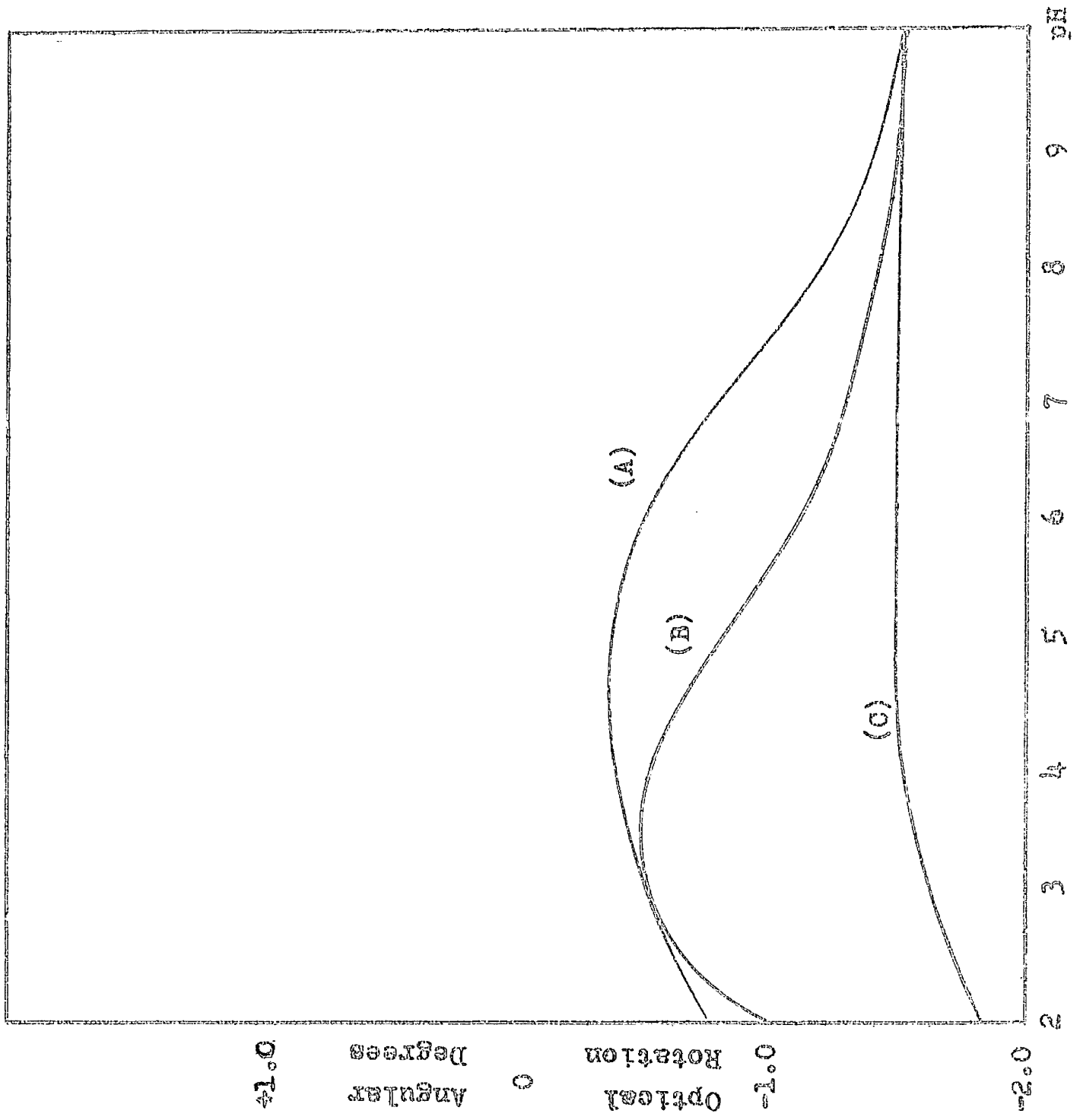


FIG. 4. - Optical Rotation plotted against pH for:

(A) 2 x 10^{-2}M sodium tungstate and 4 x 10^{-2}M L(-)mandelic acid.

(B) 2 x 10^{-2}M sodium tungstate, 4 x 10^{-2}M L(-)mandelic acid and tiron.

(C) 4 x 10^{-2}M L(-) Mandelic acid.

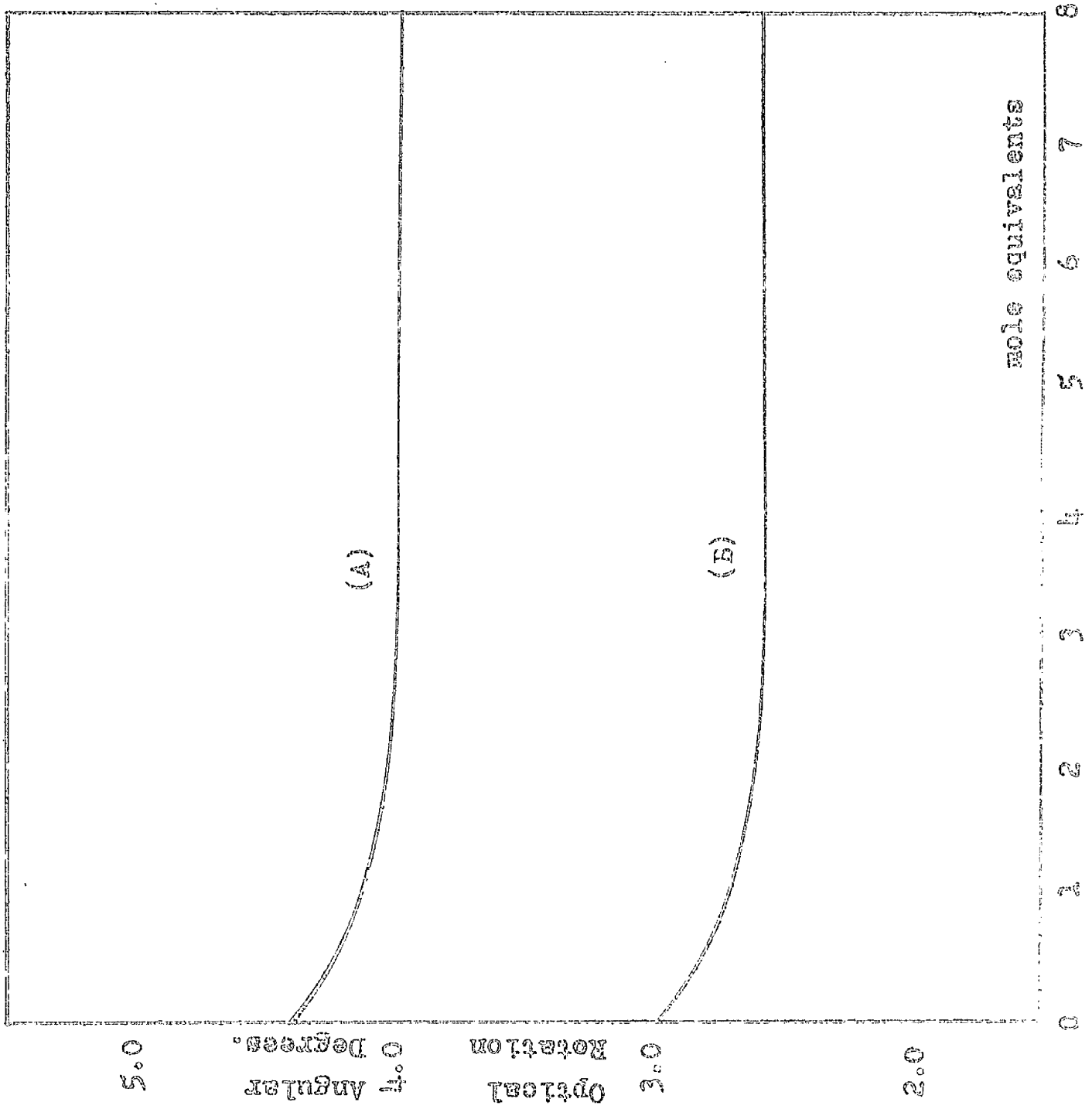


FIG. 5. - Optical rotation plotted against mole equivalent of added substance, at pH of 4.2.

(A) M Oxalic acid added to 4 x 10^{-2}M D(+) tartratomolybdate

(B) M Oxalic acid added to 4 x 10^{-2}M D(+) tartratotungstate.

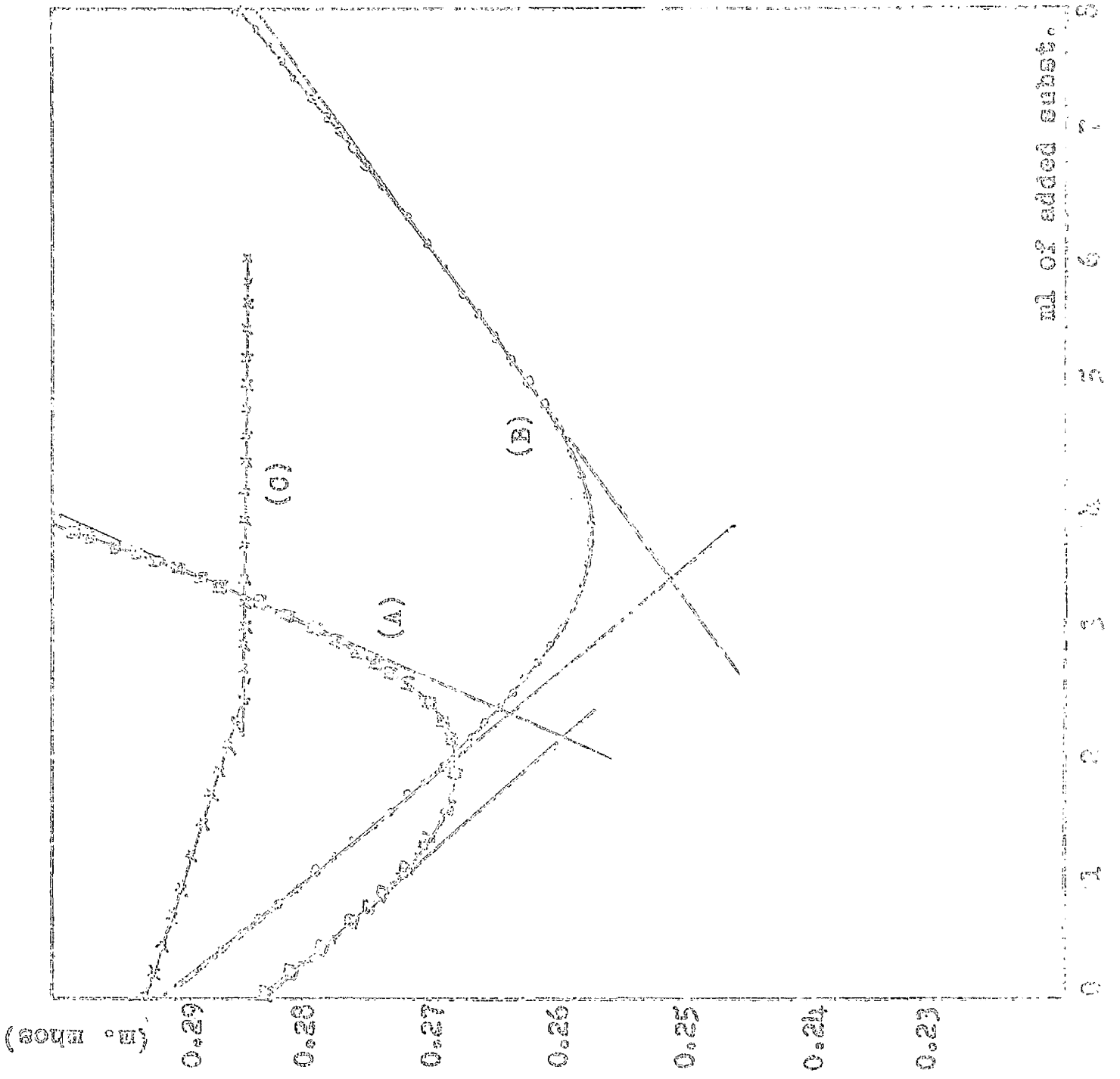


FIG. 6. Conductivity (in m.mhos) plotted against ml of 4×10^{-2}M compounds added to 1×10^{-3}M sodium molybdate: (A) trans-aconitic acid. (B) Itaconic acid. (C) D(+) Mannose.

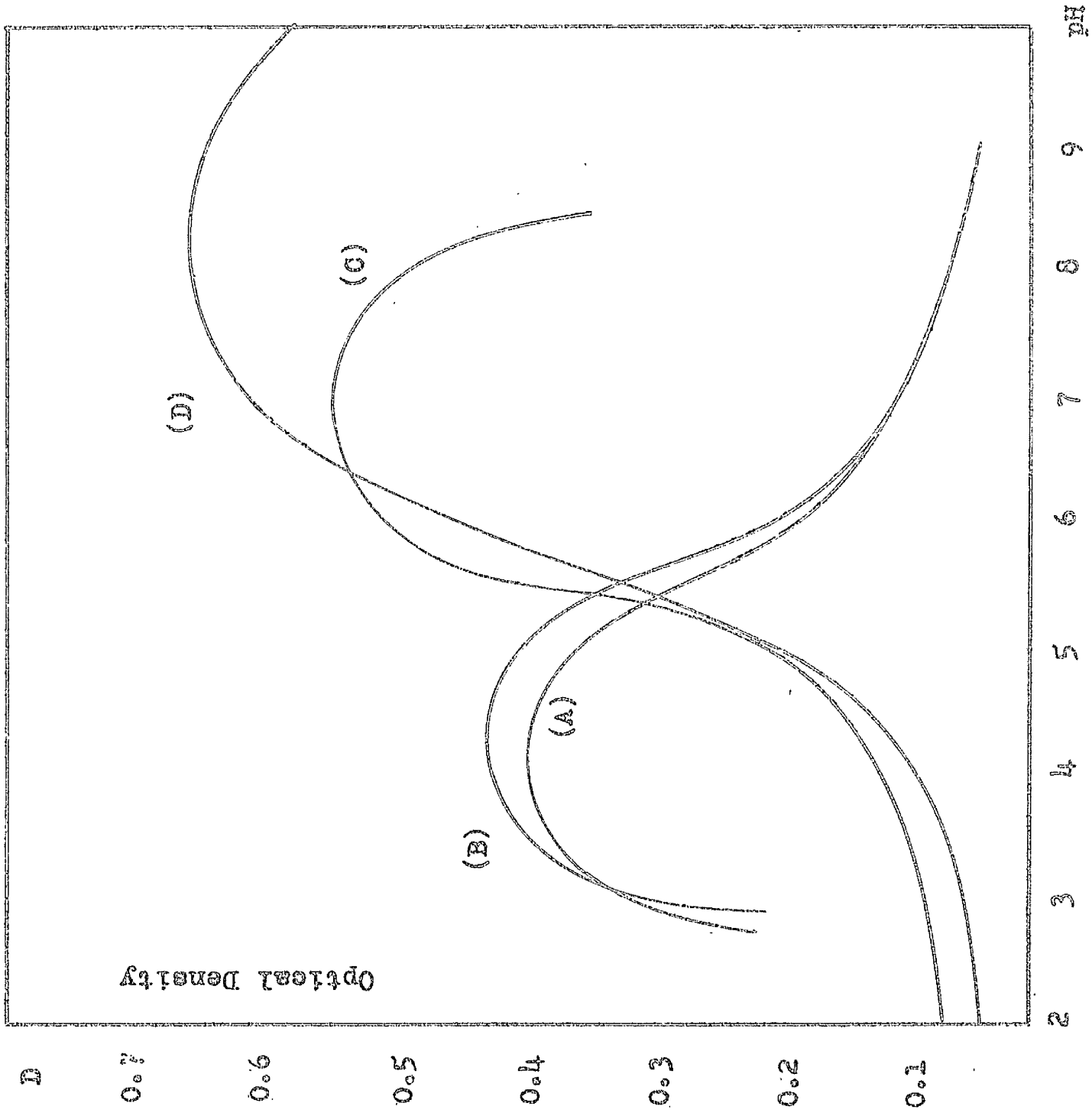


FIG. 7. - Optical density at 425 mμ plotted against pH for:
(A) 4×10^{-4}M sodium molybdate and trans-aconitic acid, and 8×10^{-4}M tiron.
(B) 4×10^{-4}M sodium molybdate and 8×10^{-4}M tiron.
(C) 4×10^{-3}M sodium tungstate and trans-aconitic acid, and 8×10^{-4}M tiron.
(D) 4×10^{-4}M sodium tungstate and 8×10^{-4}M tiron.

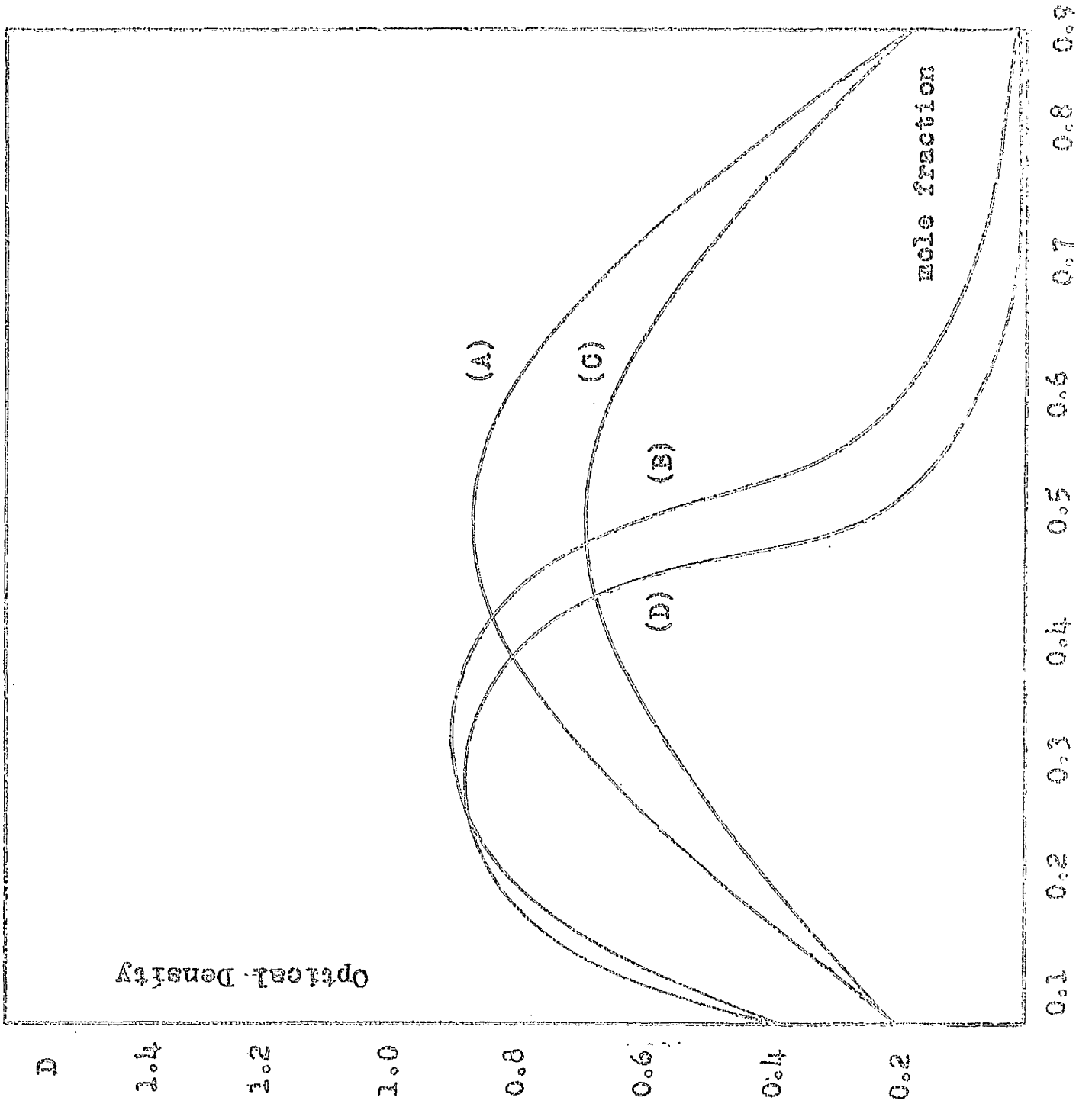


FIG. 8. - Optical Density at 425 mμ plotted against molar fraction of trans-aconitic acid complex at pH 4.5.

(A) 1×10^{-2}M trans-aconitic acid - molybdate and 1×10^{-2}M tiron.

(B) 1×10^{-1}M transaconitic acid - tungstate and 1×10^{-1}M tiron.

(C) 1×10^{-2}M itaconic acid - molybdate and 1×10^{-2}M tiron

(D) 1×10^{-1}M itaconic acid tungstate and 1×10^{-1}M tiron.

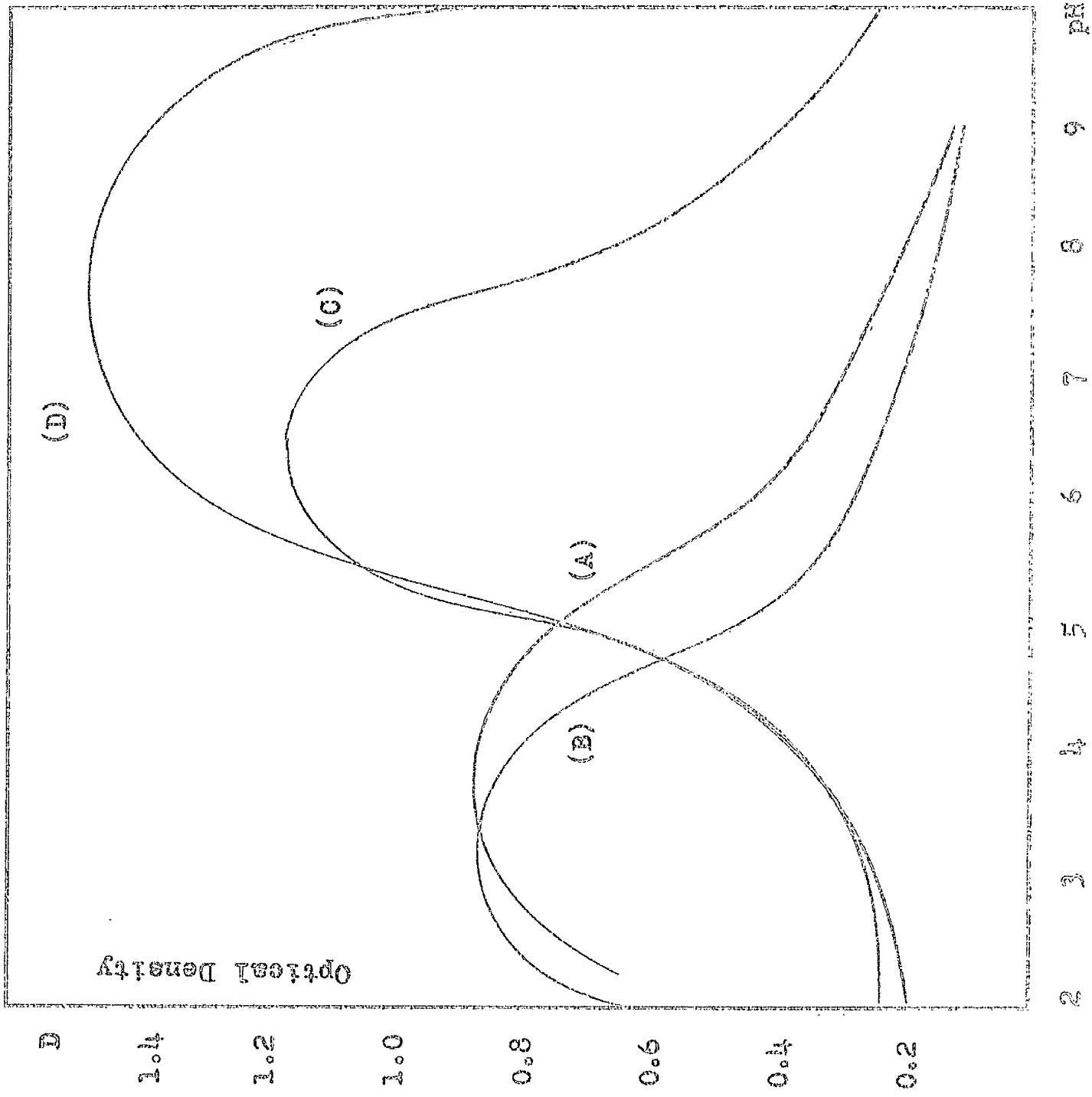


FIG. 9. - Optical Density plotted against pH for:

(A) 8 x 10^{-4}M sodium molybdate and itaconic acid, and 16 x 10^{-4}M tiron

(B) 8 x 10^{-4}M sodium molybdate and 16 x 10^{-4}M tiron

(C) 8 x 10^{-3}M sodium tungstate and itaconic acid, and 16 x 10^{-3}M tiron

(D) 8 x 10^{-3}M sodium tungstate and 16 x 10^{-3}M tiron.

EXPERIMENTAL: SECTION TWO:-

Single Ligand and Hetero Complexes With Molybdate and Tungstate Ions Involving Sugars.

§2.1 Complex with D(+) Mannose and the Corresponding Hetero Complexes with Tiron.

(i) Conductivity Plot for the Complex with D(+) Mannose: The existence of the 1:1 molybdate: sugar complex claimed by Spence and Kiang[66] on the basis of optical rotation experiments was confirmed by means of conductivity measurements. Measurement of the changes in conductivity produced by the addition of 0.04M D(+) mannose to a 100 ml. sample of 0.001M sodium molybdate showed that a break occurred in the plot after the addition of 2.5 ml. of sugar i.e. at the point where the amount of D(+) mannose added was correct for the formation of a 1:1 complex (graph 6c).

(ii) Complexes with both D(+) Mannose and Tiron.

(a) Variation of Optical Density with pH: 1 ml. each of 0.2M sodium molybdate and D(+) mannose were mixed with 2 ml. 0.2M tiron and made up to 100 ml. 10 ml. samples were adjusted to pH values varying from 2 to 10 and diluted five-fold, the pH being checked after dilution. The values of optical density measured at 425 mμ were plotted against pH and compared with those for the tiron complex alone (graphs 10a and b respectively). The solutions used for the tungstate analogue and tiron complex were more concentrated by a factor

five (graphs 10c and d respectively).

(b) Variation of Optical Rotation with pH: Results could be obtained for both molybdate and tungstate complexes by using a 10 cm. tube for the sample (as opposed to 20 cm.) and a mercury lamp as the source of illumination. The solutions used were 0.002M with respect to the metallic ions, and the variation of optical rotation with pH for the hetero molybdate complex, the molybdate-mannose and the corresponding tungstate complexes plotted on graphs 11a to d respectively. Graph e shows the optical rotation of D(+) mannose at different pH values.

(c) Stoichiometry - The Job Plot: Equal quantities of 0.2M sodium molybdate and D(+) mannose were mixed (2.5ml.) and made up to 50 ml. To 1ml. to 9ml. portions of this complex were added respectively 9 ml. to 1 ml. portions of 0.01M tiron, the samples made up to 50 ml. at pH = 4.0 and the values of optical density measured at 425 mμ. The results were plotted against mole fraction of the mannose complex to give a graph with maximum at 0.5. For the tungstate complex 5 ml. of each of 0.2M sodium tungstate and D(+) mannose were mixed and diluted to 50 ml. 0.02M tiron was added to portions of the mannose complex in the

same proportions as for the molybdate complex, each sample being made up to 50 ml. at pH = 5.5 and the values of optical density measured. On plotting the results against mole fraction of mannose complex the maximum was found to be at 0.33.

g.2.2 Complexes with D(+) Mannose and D(+) Tartaric Acid

(i) Experiments with D(+) Tartaric Acid.

(a) Variation of Optical Rotation with PH: Nine samples were prepared containing 2.5 ml. of each of the reagents: sodium molybdate, D(+) mannose and D(+) tartaric acid mixed and made up to 50 ml. at pH values in the range pH = 2 to 10. On measuring the values of optical rotation, plotting th. against pH(graph 12a) and comparing them with those for the tartrato complex alone (graph 12b) it was found that within the limits of experimental error the graphs were coincident. Using the same concentration of reagents the same was found t. be true for the tungstate complex (graphs 12c and d).

(b) Stoichiometry - The Corrected Job Plot: 0.08M D(+) tartaric acid in the proportions 4.5 ml.: 0.5ml..... 0.5 ml 4.5 ml was mixed with 0.08M sodium molybdate-D(+) mannose complex and each sample made up to 25 ml. after pH adjustment to 4.5. Compensating solutions containing 4,3,2 and 1 ml. of

the acid were prepared, diluted and adjusted to pH = 4.5 as before, whence the peak of the corrected plot of optical rotation against mole fraction of the sugar complex was found to lie at 0.5. The same concentration of reagents for the tungstate complex, also produced a peak at 0.5.

(ii) Experiments with Meso-Tartaric Acid.

(a) Variation of Optical Rotation with pH: Equal quantities of sodium molybdate, D(+) mannose and meso-tartaric acid (7.5 ml. 0.2M) were mixed and nine samples thus prepared each made up to 50 ml. after pH adjustment. Comparison of the plot of their optical rotation values against pH (graph 13a) with that for the D(+) mannose complex revealed that the presence of the meso-tartaric acid reduced the optical activity of the D(+)mannose to the value it has when uncomplexed (graph 13b). The same effect was observed with the tungstate solutions the quantities of materials dissolved in each of the 50 ml. samples being 5 ml. of 0.2M reagents (graphs 13 c and d).

(b) Stoichiometry - The Corrected Job Plot: 10 ml. 0.2M sodium molybdate and the same amount of meso-tartaric acid were mixed and made up to 25 ml. 10 ml. 0.2M D(+) mannose was also made up to 25 ml. and the two solutions mixed in the proportions 0.5 ml.: 4.5 ml. ..... 4.5ml.: 0.5ml., each

sample being made up to 25 ml. after pH adjustment to 4.5. Four compensating solutions similarly treated, containing 4,3,2 and 1 ml. of the sugar were prepared. The corrected plot of optical rotation against mole fraction of the tartrato complex showed a steadily decreasing value. A steady decrease was also obtained for the tungstate analogue, using the same concentration of reagents.

§2.3 Complexes with D(-) Ribose and with Tiron

(a) Variation of Optical Density with pH: To 1 ml. of each of 0.2M sodium molybdate and D(-) ribose mixed, was added 2 ml. 0.2M tiron and the whole made up to 100 ml. Nine 10 ml. samples were each made up to 50 ml. after pH adjustment The resultant values of optical density were measured at 425 mμ plotted against pH and compared with those for the tiron complex alone (graphs 11a and b respectively).

(b) Variation of Optical Rotation with pH: Because of the intensity of colour of the solutions it was not possible to obtain any values from optical rotation experiments.

(c) Stoichiometry - The Job's Plot: Samples of 0.01M sodium molybdate-D(-)ribose complex were mixed in the proportions 1 ml.: 9 ml....9ml.:1ml. with 0.01M tiron and each sample made up to 50 ml. at pH = 4.0. The values of optical density at

425 mu. were plotted against mole fraction of the sugar complex to produce a graph which possesses a maximum at 0.5. Using solutions of twice the concentration at pH = 5.5 it was found that the peak of optical density for the tungstate complex lay at 0.33.

§2.4 Complexes with D(-) Ribose and with D(+) Tartaric Acid.

(i) Experiments with D(+) Tartaric Acid

(a) Variation of Optical Rotation with pH: Nine samples were prepared containing equal quantities of the three reagents: sodium molybdate, D(-) ribose and D(+) tartaric acid (2.5 ml. 0.2M), the samples being adjusted to pH values from 2 to 10 and made up to 50 ml. each. On comparing the values of optical rotation (graph 15a) with those for the tartrate complex (15b) it was found that within the limits of experimental error the two graphs were coincident. Using the same concentration of reagents the same was found to be true for the tungstate complex (graphs 15c and d).

(b) Stoichiometry - The Corrected Job Plot: For both molybdate and tungstate complexes 10 ml. of 0.2M sodium molybdate (or tungstate)was mixed with the same quantity of D(-) ribose and made up to 25 ml. To nine portions of this solution was added 0.08M D(+) tartaric acid in the proportions:

0.5ml. molybdate (or tungstate)/D(-) ribose: 4.5 ml. 0.08M D(+) tartaric acid ..... 4.5 ml. sugar complex: 0.5 ml. tartaric acid, each sample being made up to 50 ml. after pH adjustment to 4.5 in the case of the molybdate and pH=6 for the tungstate. Compensating solutions were similarly prepared containing 4, 3, 2 and 1 ml. of the acid. The resultant corrected plots possessed maxima at 0.5 for both molybdate and tungstate solutions.

(ii) Experiments with Meso-Tartaric Acid.

(a) Variation of Optical Rotation with pH: 7.5 ml. of each of 0.2M sodium molybdate(or tungstate), meso-tartaric acid and D(-) ribose were mixed in nine samples, each being made up to 25 ml. after pH adjustment from 2 to 10. On plotting the values of optical rotation of these specimens against pH it was found that in both cases the introduction of the meso-tartaric acid reduced the optical activity of the D(-) ribose to the value it has when uncomplexed (graph 16a refers to the hetero molybdate solutions 16b the molybdate-D(-) ribose, 16c and d the corresponding tungstate solutions).

(b) Stoichiometry - The Corrected Job Plot: With 25 ml. of 0.2M sodium molybdate there was mixed the same quantity of

meso-tartaric acid. To portions of the tartrato complex was added 0.1M D(-) ribose in the proportions 1 ml. complex: 9 ml. sugar ..... 9 ml. complex: 1 ml. sugar, the pH values adjusted to 5.5 and the samples made up to 25 ml. each. The graph of optical rotation gainst pH shows a shallow minimum at 0.5 whereas the corresponding graph for the tungstate analogue is simply a smooth curve. The samples used for the plot, which were mixed in the same proportions as for the molybdate system and diluted to the same degree, were taken from a solution containing 20 ml. of 0.2M sodium tungstate mixed with the same amount of meso-tartaric acid and made up to 50 ml. The other reagent was 0.08M D(-) ribose.

§2.5 Complexes with L(-) Sorbose

On the basis of paper-ionophoresis experiments Bourne, Hutton and Weigel[93] claimed the existence of a 1:1 molybdate: L(-) sorbose complex. The following experiments confirm this.

(a) Variation of Optical Rotation with pH: Nine 50 ml. samples of pH form 2 to 10 were prepared containing equal quantities of sodium molybdate (or tungstate) and L(-) sorbose (10 ml. 0.8M). On plotting the values of optical rotation against pH it was found that the presence of either

molybdate or tungstate strongly influenced the activity of the sugar in the region of pH = 5.5 for the molybdate and pH = 7.0 for the tungstate. For the sugar alone the value of optical rotation was -2.37 angular degrees but in the presence of the molybdate it was -4.65 angular degrees (at pH = 6.5) and - 3.75 angular degrees at pH = 7.5 in the presence of tungstate (graphs 17a - e).

(b) Stoichiometry - The Job's Plot: For both molybdate and tungstate complexes quantities of 0.2M sodium molybdate (or tungstate) and L(-) sorbose were mixed in the proportions 4 ml. molybdate: 36 ml. sugar ..... 36 ml. molybdate: 4 ml. sugar and each sample made up to 50 ml. after pH adjustment to 4.5 in the case of the molybdate and 7.0 for the tungstate. In both cases a pronounced minimum was obtained at 0.5 in the plots of optical rotation against mole fraction of metal ion indicating 1:1 complexes.

§2.6 Hetero Complexes with L(-) Sorbose and with Tiron

(a) Variation of Optical Density with pH: Comparison of the plot of optical density against pH for the hetero complex of sodium molybdate with tiron and with L(-) sorbose with that for the tiron complex alone (graphs 14c and d respectively) indicates that the two curves, within the limits of

experimental error, are identical. For these graphs a 100 ml. sample was prepared containing 10 ml. each of 0.2M sodium molybdate and L(-) sorbose and 20 ml. 0.2M tiron. 5 ml. samples were diluted ten-fold after the requisite pH adjustments had been made.

(b) Stoichiometry - The Job's Plot: 10 ml. of 0.2M sodium molybdate was mixed with 10 ml. 0.2M L(-) sorbose and made up to 100 ml.. To samples containing 1 ml. to 9 ml. of the complex were added respectively portions of 0.02M tiron in the quantities 9 ml. to 1 ml. each sample being made up to 50 ml. at pH = 4.5. On plotting optical density against mole fraction of the L(-) sorbose complex the peak was found to be at 0.5.

For the tungstate complex 50 ml. 0.2M sodium tungstate was mixed with 50 ml. of 0.2M L(-) sorbose. 0.1M tiron was prepared and the two solutions mixed in the proportions 2ml.: 18 ml. .....18 ml.: 2ml. each sample being made up to 50 ml. after pH adjustment to 7.0. The peak was found to be at 0.33.

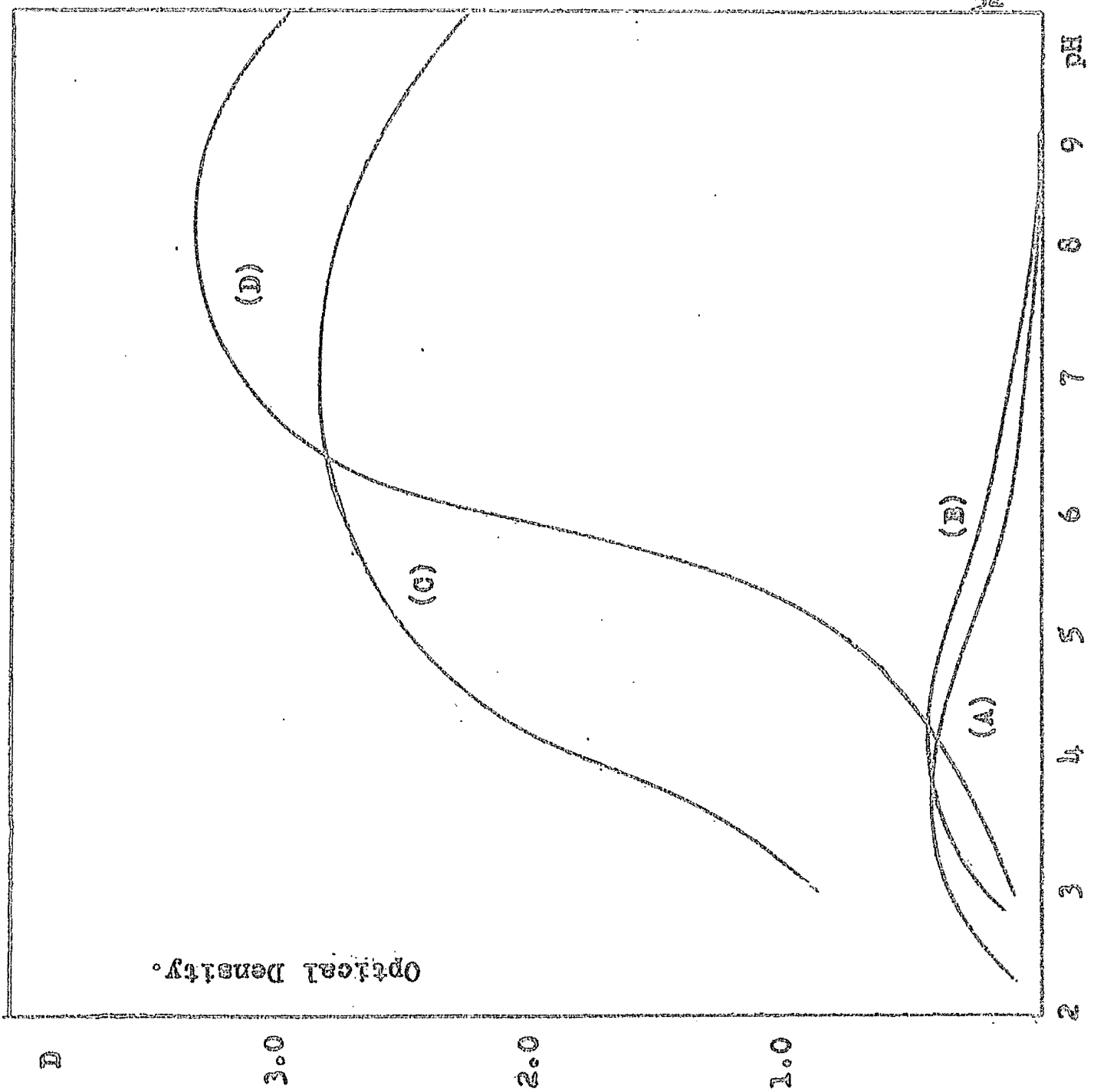


FIG. 10. - Optical Density at 425 mμ plotted against pH for:
(A) 4×10^{-4}M sodium molybdate and D(+) mannose, and 8×10^{-4}M tiron
(B) 4×10^{-4}M sodium molybdate and 8×10^{-4}M tiron.
(C) 2×10^{-3}M sodium tungstate and D(+) mannose, and 4×10^{-3}M tiron.
(D) 2×10^{-3}M sodium tungstate and 4×10^{-3}M tiron.

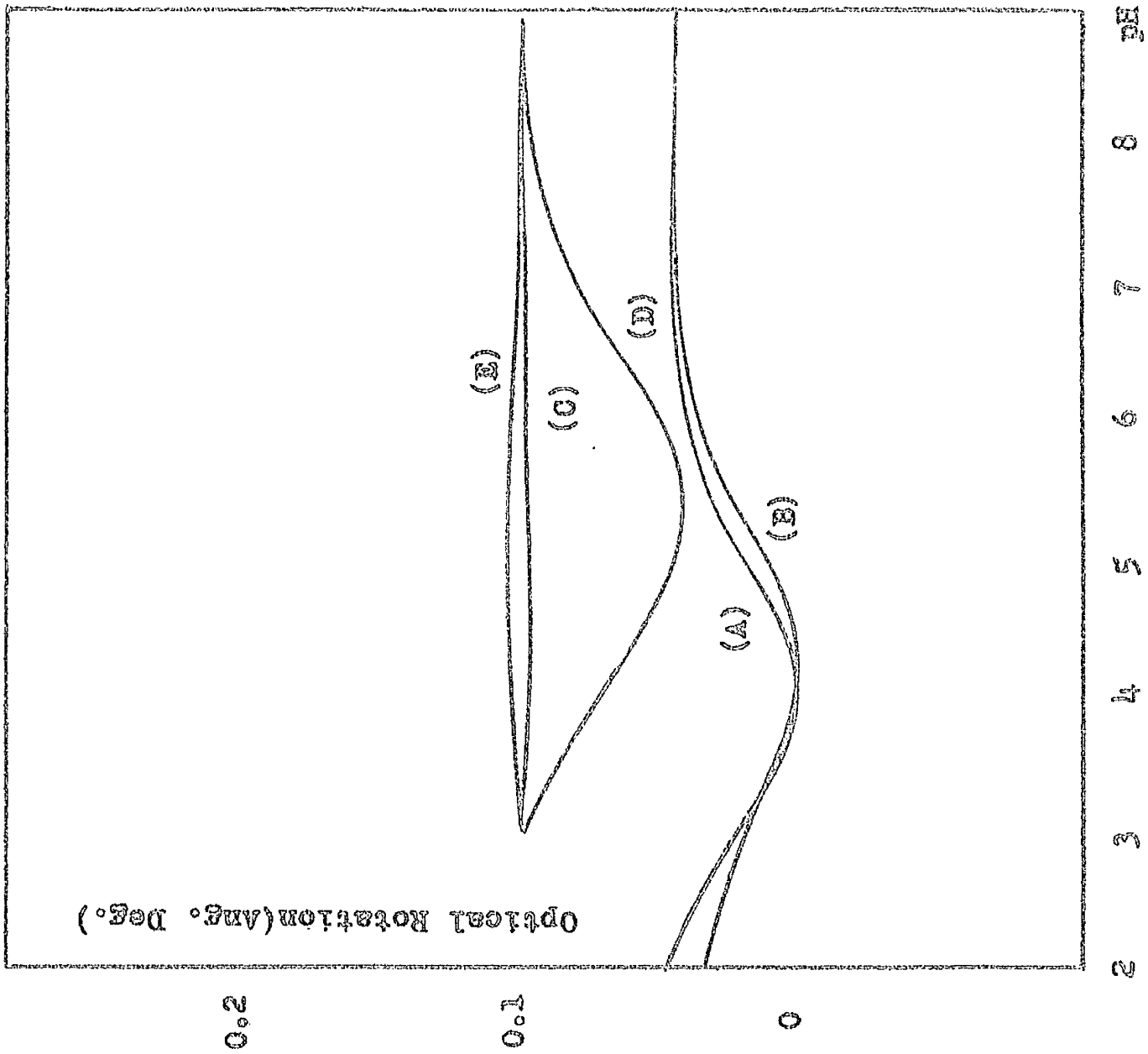


FIG. 11. - Optical Rotation plotted against pH for:
(A) 4×10^{-4}M sodium molybdate and D(+) mannose, and 8×10^{-4}M tiron.
(B) 4×10^{-4}M sodium molybdate and D(+) mannose.
(C) 2×10^{-3}M sodium tungstate and D(+) mannose, and 4×10^{-3}M tiron.
(D) 2×10^{-3}M sodium tungstate and D(+) mannose.
(E) 2×10^{-3}M D(+) mannose.

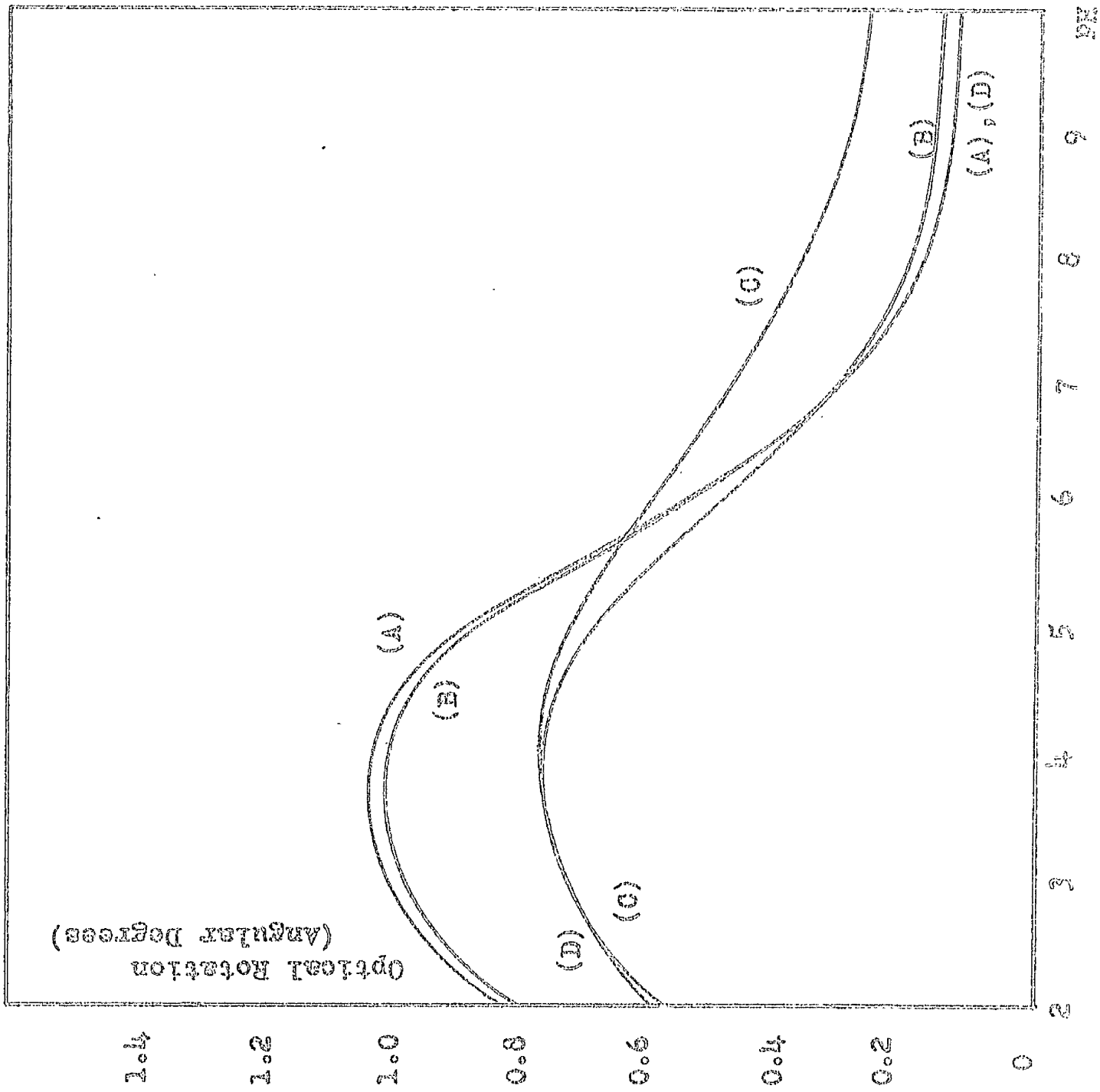


FIG. 12. - Optical Rotation plotted against pH for:

(A) 1 x 10^{-2}M sodium molybdate, D(+) mannose and D(+) tartaric acid.

(B) 1 x 10^{-2}M sodium molybdate and D(+) tartaric acid.

(C) 1 x 10^{-2}M sodium tungstate, D(+) mannose and D(+) tartaric acid.

(D) 1 x 10^{-2}M sodium tungstate and D(+) tartaric acid.

FIG. 13. - Optical Rotation plotted against pH for:

(A) 3 x 10^{-2}M sodium molybdate, D(+) mannose and meso-tartaric acid.

(B) 3 x 10^{-2}M sodium molybdate and D(+) mannose.

(C) 2 x 10^{-2}M sodium tungstate, D(+) Mannose and meso-tartaric acid.

(D) 2 x 10^{-2}M sodium tungstate and D(+) mannose.

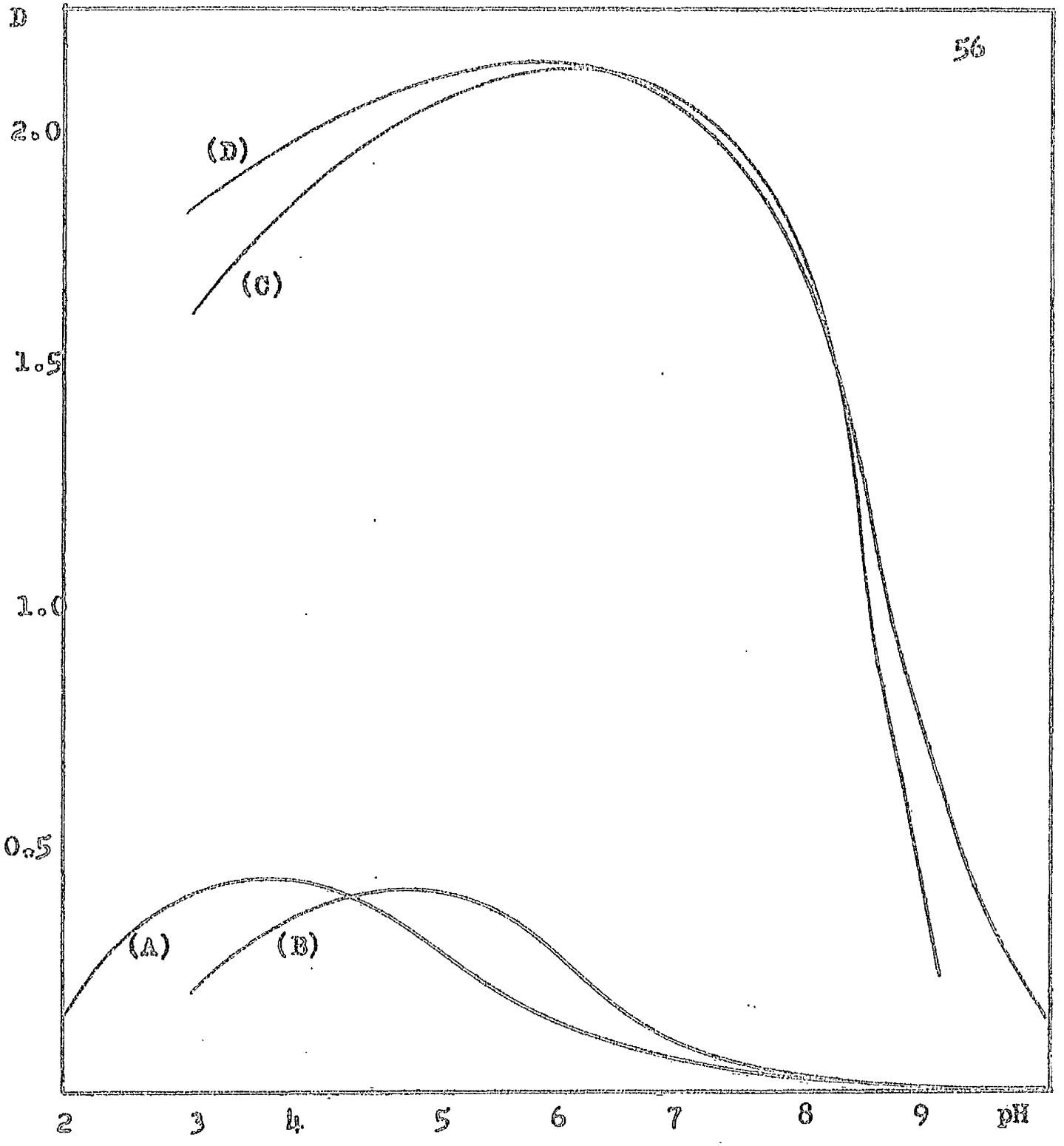


FIG. 14. - Optical Density at 425 mμ plotted against pH for:
(A) 4 x 10^{-4}M sodium molybdate and D(-) ribose, and 8 x 10^{-4}M tiron.
(B) 4 x 10^{-4}M sodium molybdate and 8 x 10^{-4}M tiron.
(C) 2 x 10^{-2}M sodium molybdate and L(-) sorbose, and 4 x 10^{-2}M tiron.
(D) 2 x 10^{-2}M sodium molybdate and 4 x 10^{-2}M tiron.

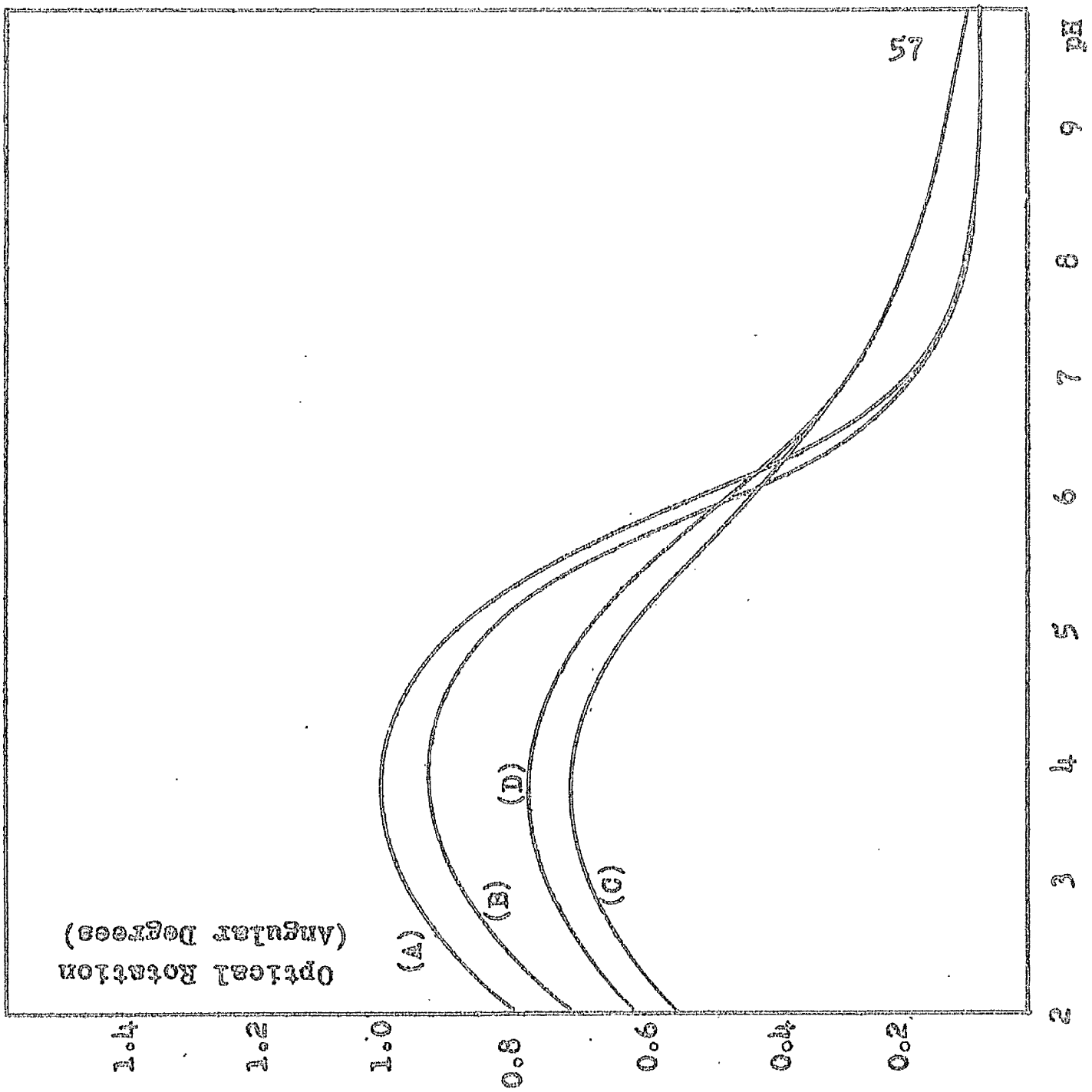


FIG. 15. - Optical Rotation plotted against pH for:

(A) 1 x 10^{-2}M sodium molybdate, D(-) ribose and D(+) tartaric acid.

(B) 1 x 10^{-2}M sodium molybdate and D(+) tartaric acid.

(C) 1 x 10^{-2}M sodium tungstate, D(-) ribose and D(+) tartaric acid.

(D) 1 x 10^{-2}M sodium tungstate and D(+) tartaric acid.

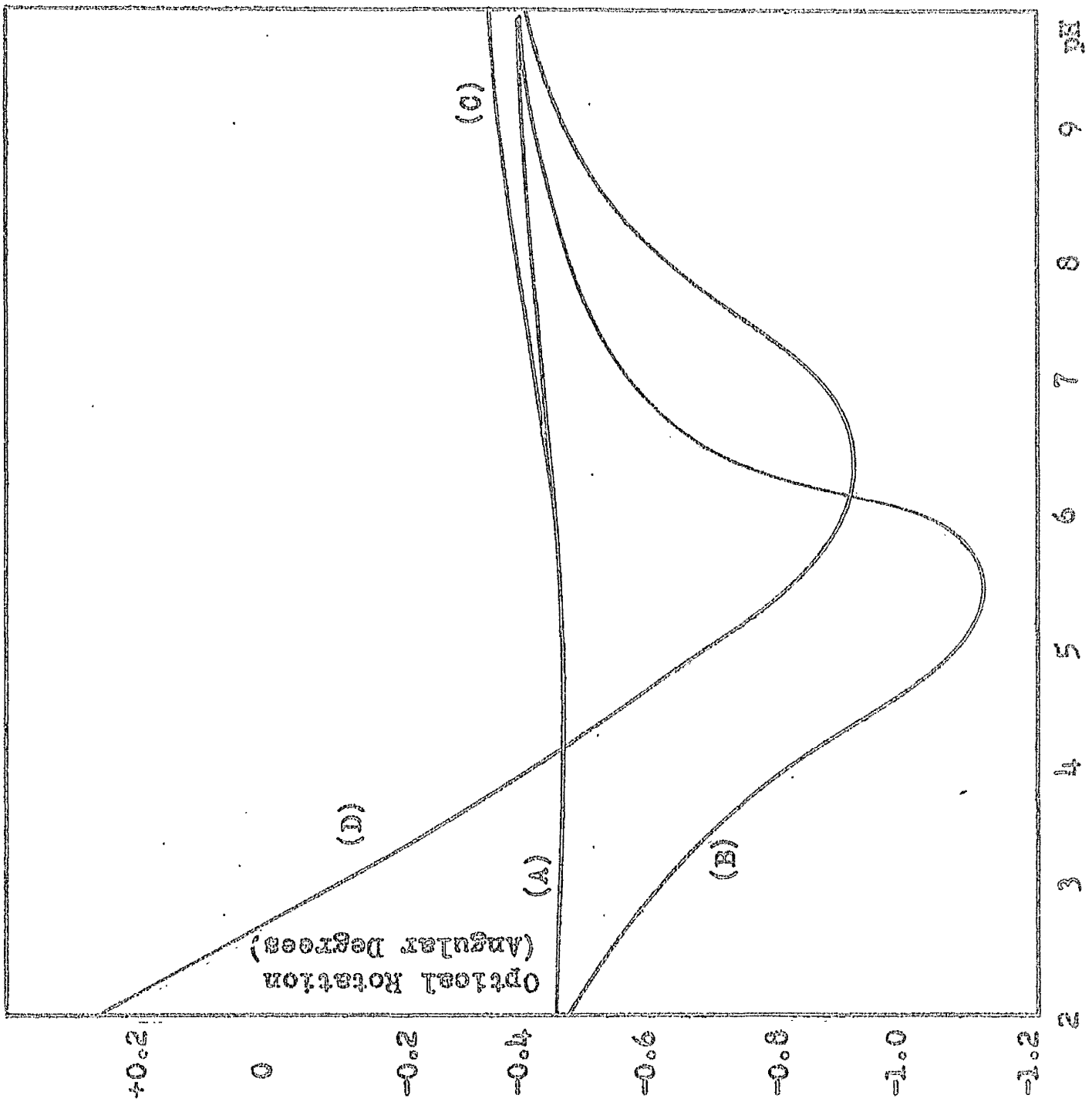


FIG. 16. - Optical Rotation plotted against pH for:

(A) 6 x 10^{-2}M sodium molybdate, D(-) ribose and meso-tartaric acid.

(B) 6 x 10^{-2}M sodium molybdate and D(-) ribose.

(C) 6 x 10^{-2}M sodium tungstate, D(-) ribose and meso-tartaric acid.

(D) 6 x 10^{-2}M sodium tungstate and D(-) ribose.

FIG. 17. Optical Rotation plotted against pH for:
(A) 1.6×10^{-1} M sodium molybdate and L(-) sorbose.
(B) 1.6×10^{-1} M sodium tungstate and L(-) sorbose.
(C) 1.6×10^{-1} M L(-) sorbose.

2710

EXPERIMENTAL: SECTION THREE:-

Single Ligand and Hetero Complexes With Molybdate and Tungstate Ions Involving Polyhydroxy Molecules.

g3.0 Single Ligand and Hetero Complexes Involving Polyhydroxy Molecules.

g3.1 Complex with D - Mannitol and with Tiron

(a) Stoichiometry-The Job Plot: 10 ml. 0.2M sodium molybdate and 5 ml. 0.2M D - mannitol were mixed and made up to 100 ml. 100 ml. of 0.02M tiron was also prepared and the solutions mixed in the proportions 1 ml.: 9 ml..... 9 ml.: 1ml., each sample being made up to 50 ml. and the pH adjusted to 4.5. The peak of the graph of optical density against mole fraction of the mannitol complex was found to lie between 0.4 and 0.5, i.e. a complex was formed with the ratio MoO_4: mannitol:Tiron = 2:1:2.

0.24M tiron was added in portions to 0.24M sodium tungstate-mannitol complex, the ratio of components being 18 ml.:2 ml. ..... 2ml.: 18 ml. Each sample was again made up to 50 ml. at pH = 4.5 and the values of optical density from them used to produce a Job Plot with a peak at 0.33 i.e. the tiron was complexed at the expense of the mannitol.

(b) Variation of Optical Density with pH: With a hetero complex containing both mannitol and tiron there arises the difficulty that it is not possible to obtain comparative plots of optical density against pH for a tiron molybdate or

tungstate complex possessing a 1:1 ratio of components. Accordingly measurements could only be taken for the system $(MoO_4^{2-})_s/(D\text{ - mannitol})_1/(Tiron)_s$ (graph 18a). 10 ml. 0.2M sodium molybdate and 5 ml. 0.2M D - mannitol were mixed with 10 ml. 0.2M tiron, the resultant solutions being made up to 100 ml. 5ml. samples were diluted ten-fold after the appropriate pH adjustments had been made and the values of optical density plotted against pH.

Due to the weakness of the optical rotation of the mannitol no information could be obtained concerning possible effects upon the optical activity of the mannitol.

§2.2 Complex with D-Sorbitol

(a) Conductivity Plot: Against a 100 ml. sample of 0.001M sodium molybdate was titrated 0.04M D - sorbitol and the resultant values of conductivity noted. It was found that the break in the graph of conductivity against ml. of sorbitol added occurred after the addition of 1 ml. of D - sorbitol, indicating that the ratio of components is $2(MoO_4^{2-}):1D(-)$ sorbitol. These results confirm the work of Angus.[79]

(b) Stoichiometry - The Corrected Job Plot: Quantities of 0.2M sodium molybdate and D - sorbitol were mixed in the proportions 4 ml. molybdate: 36 ml. D - sorbitol .....36ml.

molybdate: 4ml. D - sorbitol, each sample being made up to 50 ml. with pH adjustment to 4.5. Compensating samples containing 34, 28, 22, 16, 10 and 4 ml. of sorbitol each adjusted to pH = 4.5 and made up to 50 ml. were used to determine the values of optical rotation due to the complex alone. The graph showed a peak at 0.66 indicative of a complex possessing the ratio of components $2(MoO_4^{2-})$:D - sorbitol.

For the tungstate analogue samples of molar reagents were diluted up to 50 ml. at pH = 4.5, the proportions being 2 ml. tungstate 18 ml. D - sorbitol ..... 18 ml. tungstate: 2 ml. D - sorbitol. Compensating solutions diluted to the same final pH and volume contained respectively 17, 14, 11, 8 and 5 ml. of the D - sorbitol. Again the peak at 0.66 indicated at 2:1 complex.

(c) Variation of Optical Rotation with pH: Nine 50 ml. samples at pH values from 2 to 10 were prepared containing 20 ml. 0.4M sodium molybdate mixed with 20 ml. 0.2M D - sorbitol. The optical rotation values were measured and compared with those for D - sorbitol alone (graphs 19a and b).

Where the tungstate complex is concerned the curve appears to be somewhat better defined, a minimum being observed at about pH = 7.5 (graph 19c), when molar reagents are used. The samples, finally made up to 50 ml. each at the

required pH values contained 10 ml.M sodium tungstate mixed with 5 ml. M D - sorbitol.

§2.3 Complexes with D - Sorbitol and with Tiron

(a) Stoichiometry - The Job Plot: 9 ml. - 1 ml. quantities of 0.02M tiron were respectively added to 1 ml. - 9 ml. samples of a solution of sodium molybdate - D - sorbitol complex, prepared by mixing 10 ml. 0.2M sodium molybdate with 5 ml. of 0.2M alcohol and making up the volume to 100 ml. All samples were made up to 50 ml. at pH = 4.5, the optical densities measured, and the results plotted against mole fraction, to produce a graph with maximum at 0.5 ie. the ratio of components is molybdate: D - sorbitol:tiron = 2:1:2.

50 ml. M sodium tungstate was mixed with 25 ml. M D - sorbitol and the whole made up to 100 ml. This solution was mixed with 0.5M tiron in the proportions 2 ml.:18ml.... 18ml.: 2 ml. and the samples made up to 50 ml. each at pH = 4.5. The resultant graph did not show a maximum indicative of hetero complex formation.

(b) Variation of Optical Density with pH: As with the mannitol complex it is not possible to obtain a comparative molybdate-tiron plot of optical density against pH. For the hetero complex the solution used contained 10 ml. of each of 0.2M sodium molybdate and tiron mixed with 5 ml. 0.2M D -

sorbitol. 5 ml. samples were diluted ten-fold after the sorbitol. 5 ml. samples were diluted ten-fold after the requisite adjustment had been made to the values of pH. The values of optical density are recorded in graph (26b).

§2.4 Complexes with both D - Sorbitol and D(+) Tartaric Acid.

(i) Experiments with D(+) Tartaric Acid.

(a) Stoichiometry - The Corrected Job Plot: Portions of a solution containing 40 ml. 0.4M sodium molybdate mixed with 20 ml. 0.4M D - sorbitol were mixed with samples of 0.26M D(+) tartaric acid, the proportions respectively being 1 ml.: 9 ml. ..... 9 ml.: 1 ml. acid. All samples were made up to 50 ml. at pH = 4.5. Compensating solutions containing 8,6,4 and 2 ml. of D(+) tartaric acid were similarly treated and by subtraction of their values of optical rotation from those for the hetero solutions the optical rotation values for the hetero complex alone was ascertained. The results show a peak at 0.5 in the graph of optical rotation against mole fraction of the alcohol complex, indicating the ratio of components: molybdate: D - sorbitol: D(+) tartaric acid = 2:1:2.

(b) Variation of Optical Rotation with pH: Nine 50 ml. samples at the requisite pH values were prepared containing 5 ml. each of 0.4M sodium molybdate and D(+) tartaric acid

mixed with 2.5 ml. 0.4M D - sorbitol and the values of optical rotation measured for comparison with the tartrato complex alone (graphs 18c and d respectively).

(ii) Experiments with Meso-Tartaric Acid-The Corrected Job Plot: 40 ml. M sodium molybdate and meso-tartaric acid were mixed and to portions of solution was added portions of 0.5M D - sorbitol in the proportions 2 ml. tartrato complex: 18 ml. D - sorbitol ..... 18 ml. complex: 2 ml. D - sorbitol. The solutions were each made up to 50 ml. at pH = 4.5 and by means of compensating solutions similarly prepared containing respectively 16, 12, 8 and 4 ml. D - sorbitol the values of optical rotation plotted against mole fraction of tartrato complex. This plot possessed a maximum at 0.5 indicative of the ratio of components $2(MoO_4^{2-})$: 1D - sorbitol: 2(tartaric acid).

Where the tungstate analogue was concerned the results were extremely uncertain. In the Job Plot for both D(+) tartaric acid and meso-tartaric acid experiments the optical rotation values of the Job Plot rose to values which remained constant over the mole-fraction range 0.3 - 0.5 inclusive. Accordingly no hetero tungstate complex is formed.

FIG. 18. Optical Density at 425 mμ plotted against pH for:
(A) 2 x 10^{-3}M sodium molybdate and tiron, and 1 x 10^{-3}M D-mannitol.
(B) 2 x 10^{-3}M sodium molybdate and tiron, and 1 x 10^{-3}M D-sorbitol.
Optical Rotation plotted against pH for:
(C) 4 x 10^{-2}M sodium molybdate and D(+) tartaric acid, and 2 x 10^{-2}M D-sorbitol.
(D) 4 x 10^{-2}M sodium molybdate and D(+) tartaric acid.

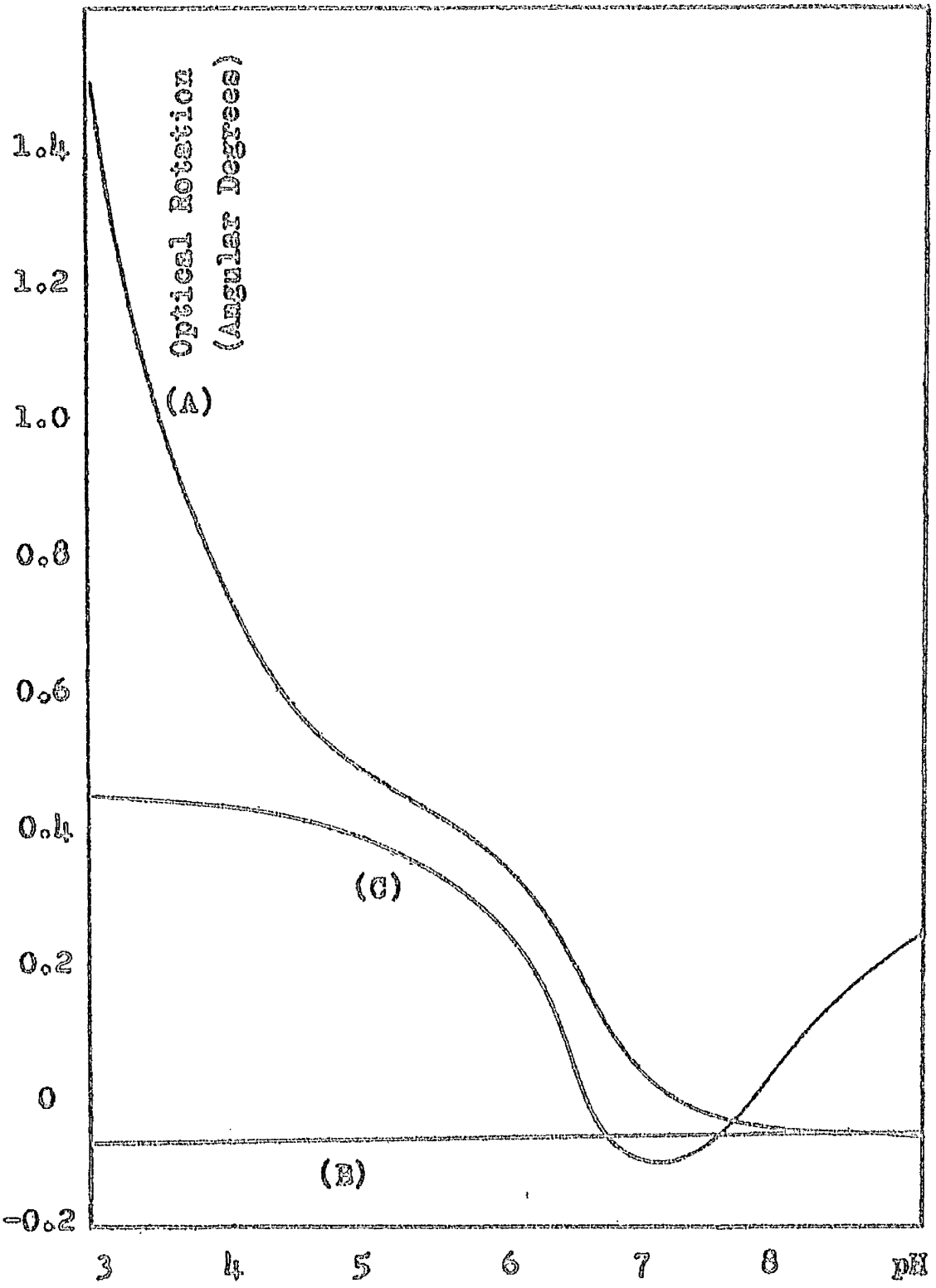


FIG. 19. Optical Rotation plotted against pH for:
(A) 16 x 10^{-2}M sodium molybdate and 8 x 10^{-2}M D-sorbitol
(B) 8 x 10^{-2}M D-sorbitol.
(C) 2 x 10^{-1}M sodium tungstate and 1 x 10^{-1}M D-sorbitol.

EXPERIMENTAL: SECTION FOUR:-

Single Ligand and Hetero Complexes With Molybdate Ion Involving Hydroxylamine.

g4.1 Complex with Hydroxylamine

(a) Variation of Optical Density with pH: Nine samples were prepared containing 10 ml. each of 0.2M sodium molybdate and hydroxylamine hydrochloride and each sample made up to 50 ml. after adjustment of pH from 2 to 10 and their optical densities measured at 425 mμ. The resultant plot of optical density against pH possessed a maximum at pH = 5.5. It was found, however, that the time taken for the solutions to finally reach equilibrium was three days, since over this period the solutions deepened in colour from orange to red until the maximum of optical density had reached twice the intensity of that measured from the solutions examined immediately on preparation. Thereafter the values of optical density remained constant (graphs 20 a, b and c).

(b) Stoichiometry - The Job Plot: Again, it was found that the definition of the peak at 0.5 corresponding to a 1:1 complex was considerable improved after three days. For these experiments 0.1M reagents were used, the solutions being mixed in the proportions 2 ml. sodium molybdate: 18 ml. hydroxylamine.... 18 ml. molybdate: 2 ml. hydroxylamine and each sample made up to 50 ml. after pH adjustment to 5.5. After

standing for three days the pH values were again checked and the optical densities measured at 425 mμ.

§4.2 Complex with D(+) Tartaric Acid and with Hydroxylamine.

(a) Variation of Optical Density with pH: Despite the fact that the optical density values for the hetero solutions are about ⅓ of those for the single ligand complex at comparable pH values the curves again show that a steady value of optical density was reached after three days. Here 90 ml. of each of 0.2M sodium molybdate, hydroxylamine hydrochloride and D(+) tartaric acid were mixed together, the reagents being added to each other in that order. Nine 30 ml. samples of the resultant solution were made up to 50 ml. each after pH adjustment to pH 2 to 10. After three days the pH values were checked and the optical density measured at 425 mμ. and plotted against pH (graph 21a, b and c).

(b) Variation of Optical Rotation with pH: Using the same samples as for the optical density measurements it was found that the values of optical rotation did not change with time, the curves for measurements taken after one hour, three days and six days being coincident not only with one another (graphs 22a, b, c respectively) but with that for the tartrato-molybdate complex alone(graph 22 d).

(c) Stoichiometry - The Job Plot: Here, too, time affected the definition of the peak, although not to the same extent as for the single ligand complex. The graphs of optical density against mole fraction of tartrato-molybdate possessed a maximum at 0.5 indicative of a 1:1:1 ratio of components. The solutions used for the measurements were prepared by mixing 0.1M reagents in the ratio 1 ml. tartrato-complex: 9 ml. hydroxylamine ..... 9 ml. tartrato-molybdate:1 ml. hydroxylamine and making up each sample to 50 ml. at pH = 5.5. The pH of the samples was rechecked at the end of the three days before measurement of optical density.

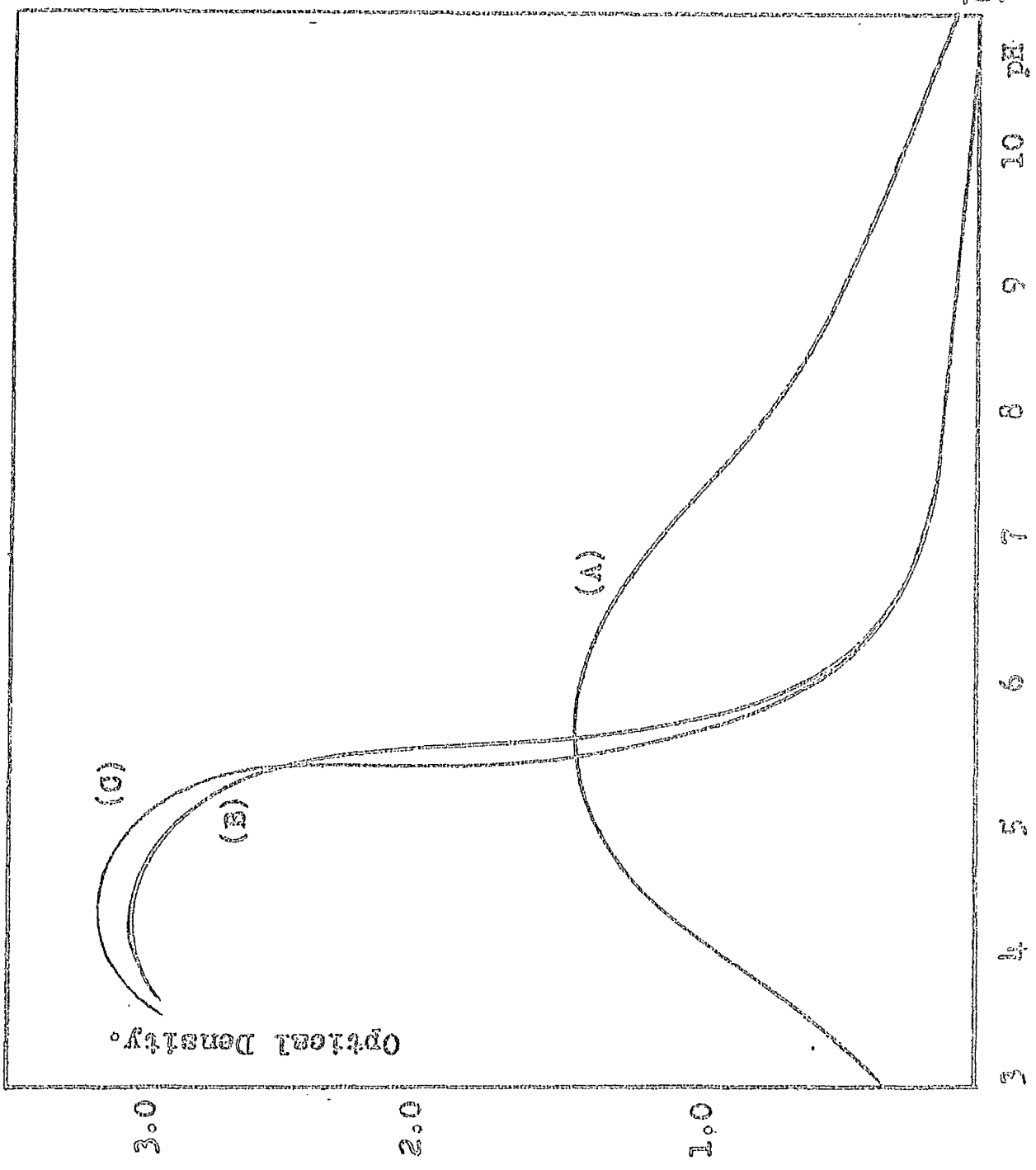


FIG 20. Optical Density at 425 mμ plotted against pH for: 4×10^{-2}M sodium molybdate and Hydroxylamine Hydrochloride

(A) One Hour after preparation.

(B) Three Days after preparation.

(C) Six Days after preparation.

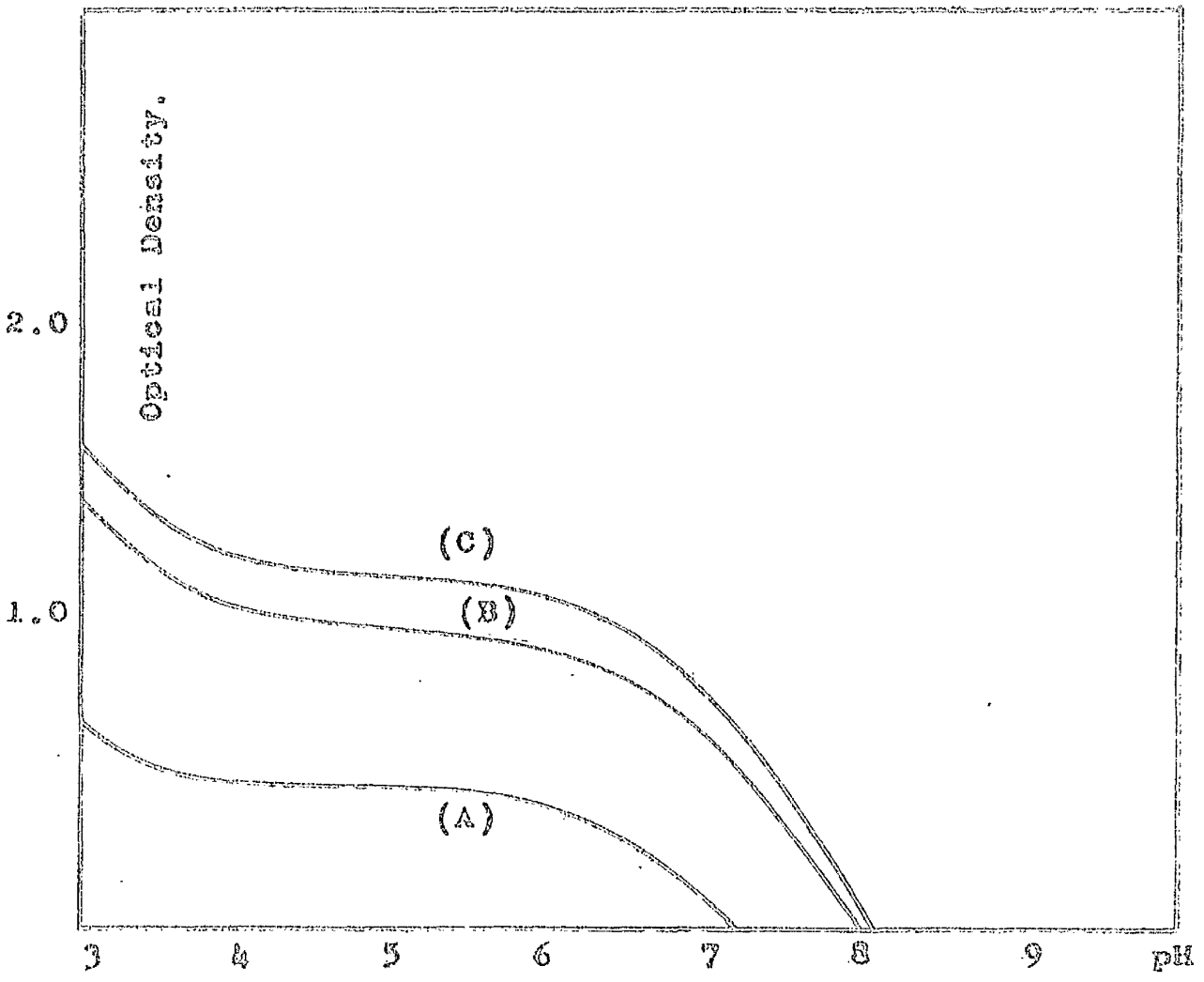


FIG. 21. Optical Density at 425 mμ plotted against pH for:
4×10^{-3}M sodium molybdate, D(+)-tartaric acid and
Hydroxylamine Hydrochloride,

(A) One Hour after preparation.

(B) Three Days after preparation.

(C) Six Days after preparation.

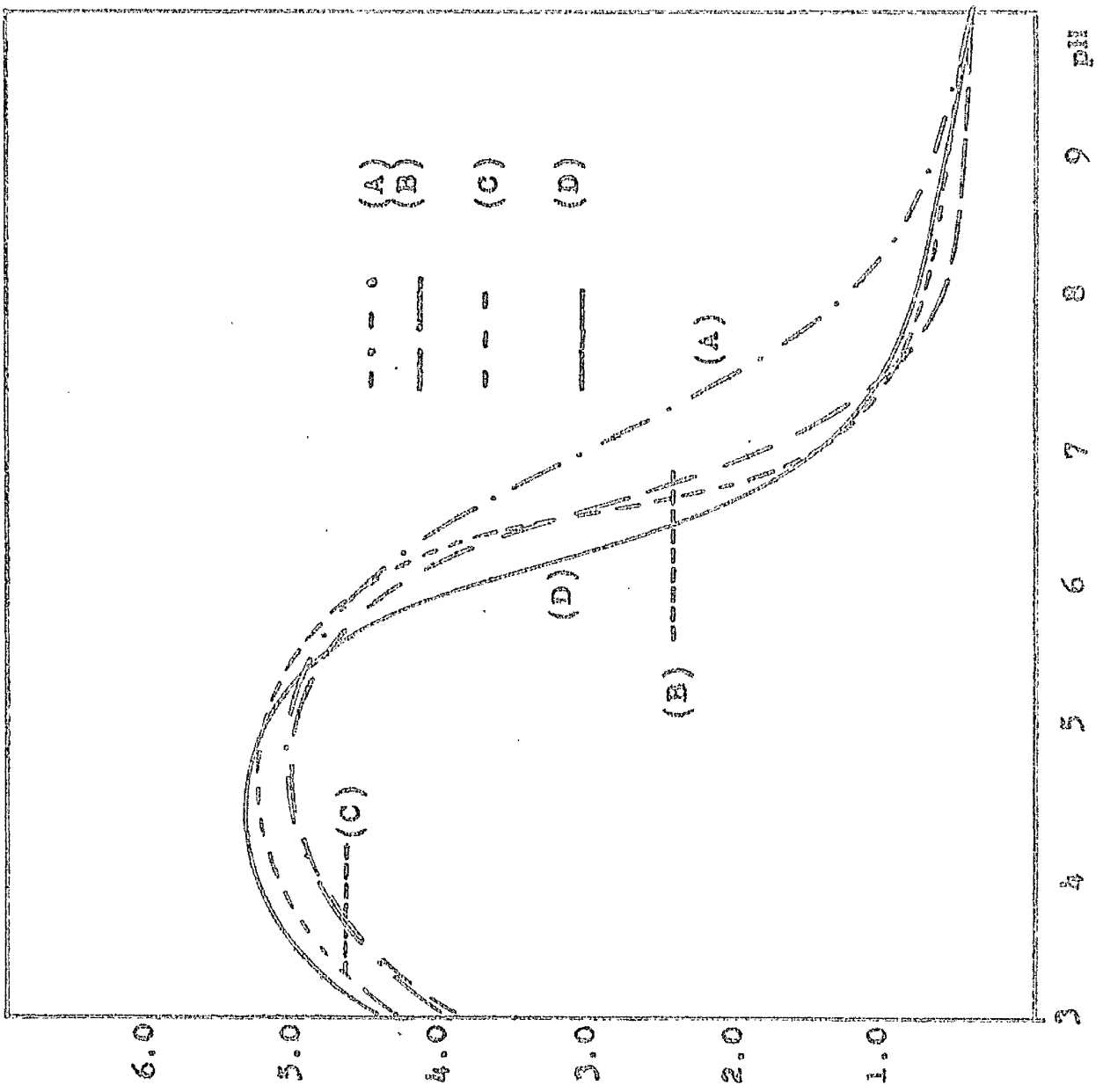


FIG. 22. Optical Rotation plotted against pH for:
4 x 10^{-3}M sodium molybdate, D(+) tartaric acid and Hydroxylamine Hydrochloride,

(A) One Hour after preparation,

(B) Three Days after preparation,

(C) Six Days after preparation,

(D) Optical Rotation plotted against pH for
4 x 10^{-3}M sodium molybdate and D(+) Tartaric acid.

§5.1 Irradiation and Refluxing of Single Ligand Complexes of Molybdate.

When solutions of tartrato and mandelato molybdate were irradiated with U.V. light for two hours they turned a deep red colour, which faded on allowing the solutions to stand overnight. That there was some form of reaction resulting in the reduction of the molybdenum by the organic ligand became evident when a smell somewhat akin to that of burnt sugar was observed to come from the tartrato complex and the smell of bitter almonds from the mandelic acid complex solutions.

Since the U.V. lamp evolved a considerable amount of heat it could not be said that these reactions were the consequense of irradiation alone, and in fact when samples of the complexes were refluxed it was found that the reactions proceeded much more rapidly and effectively. Both complex solutions turned an intense red colour, and within three hours a reddish-orange solid began to settle out from the mandelic acid complex solution. After refluxing for twenty-four hours the solutions were more or less stabilized in their coloured forms and detailed examination of them was therefore

EXPERIMENTAL: SECTION FIVE:-

THE REACTIONS OF MOLYBDATE ION COMPLEXES.

carried out.

With regards to the tartrato complex very little information could be obtained since it proved difficult to identify the organic product of the reaction. Nor could the oxidation state of the molybdenum be ascertained since interference of the organic species present in solution with the oxidizing agents employed (permanganate and ceric ammonium sulphate titrations) resulted in the end point in the titrations being very uncertain. Attention was therefore directed to the mandelic acid complex.

All samples were prepared in the manner described for the mandelato complex. 90 ml. 0.2M sodium molybdate were mixed with 180 ml. 0.2M mandelic acid and the whole made up to 300 ml. at pH = 6.5. Within one hour of commencing refluxing the solution turned deep red and within three hours had begun to deposit a reddish-orange solid, refluxing being continued for five days. The orange solid, which formed 23.44% by weight of the starting material, was filtered from the red liquid, washed with acetone and ether and dried under vaccuum. Solid and liquid were then separately examined.

50 ml. samples of the red liquid was extracted with ether, the extract washed with water and dried with anhydrous sodium

sulphate. The infrared spectrum of the extract, taken in chloroform, revealed an aromatic peak at 3.28μ, a - CHO peak at 3.45 - 3.70μ and C=C stretching vibrations at 6.25 and 6.55μ. In addition there were peaks at 9.03μ, 9.30 - 9.83 μ, 11.45μ and 11.85μ all of which are present in the spectrum of benzaldehyde, thus confirming that the smell of bitter almonds evolved from the red liquid was that of benzaldehyde. As with the tartrate solution interference of the organic matter present in solution with the oxidizing agents prevented the oxidation state of the molybdenum species in solution from being determined.

Ignition of the orange solid to MoO_3 revealed that the percentage of molybdenum was 49.81% while the percentage of hydrogen was found to be 2.09% Standard permanganate and ceric ammonium sulphate titrations indicated a valency of V. These facts are in accord with the formulation of the compound as $NaMoO_3.2H_2O$ (%Mo = 47.27%, %H = 1.98%).

Other acid complexes refluxed under similar conditions were those of lactic, citric and glycollic acids. Of the three only the first was partially reduced to molybdenum blue (a mixture of Mo(VI) and Mo(V)), the other two showing no apparent reaction.

All three sugar complexes refluxed turned an intense

red colour which on heating for three to four days became cloudy due to charring, the D(+) mannose and D-ribose complexes being refluxed at pH = 5.0 and the L-Sorbose complex at pH = 5.5. Mannitol and sorbitol complexes were reduced to molybdenum blue. The only consequence of refluxing the hydroxylamine complex of sodium molybdate was the destruction of the hydroxylamine itself as evidenced by the evolution of ammonia and the disappearance after three days of the orange colour of the complex. When repeated under an atmosphere of nitrogen the hydroxylamine reduced the sodium molybdate to molybdenum blue.

§5.2 <u>The Effects of the Presence of Various Ions on Refluxing Complex Solutions</u>.

The presence of different ions was found to influence the redox system operating between the molybdate and ligand. Sulphate ion (present as sodium sulphate) produces very little effect on the redox process, the tartrato complex still turning deep red after refluxing for three days. However, with sodium carbonate (probably in the form of a mixture of carbonate and bicarbonate) present, only a light brown colouration was observed after the same length of time while the addition

of disodium hydrogen phosphate (present as a mixture of NaH_2PO_4 and Na_2HPO_4) decreased the extent of reduction from molybdenum(V) to molybdenum blue. In all cases a quantity of the salt necessary to provide two equivalents was added to the solutions, the experiments being carried out at pH = 7.0

The refluxing of the mandelic acid complex with excess potassium nitrate or nitrite resulted in the extent of the reduction to molybdenum(V) being decreased, no orange solid being deposited. There were traces not only of nitrogen dioxide (or nitric oxide) produced from the nitrate and nitrite but also traces of ammonia.

With the tartrato-molybdate complex it was found that although a trace of ammonia was produced the solution only possessed a blue tinge in the case of the nitrate and remained colourless for the nitrite i.e. the hexavalent state of the molybdenum was stabilized by the presence of the nitrate and nitrite. Sugar complexes, on the other hand, on being refluxed at pH = 7.0 with excess potassium nitrate were not stabilized as the molybdenum(VI) complexes but were reduced, as before, to produce intensely red coloured solutions.

DISCUSSION.

§6.1 Introduction

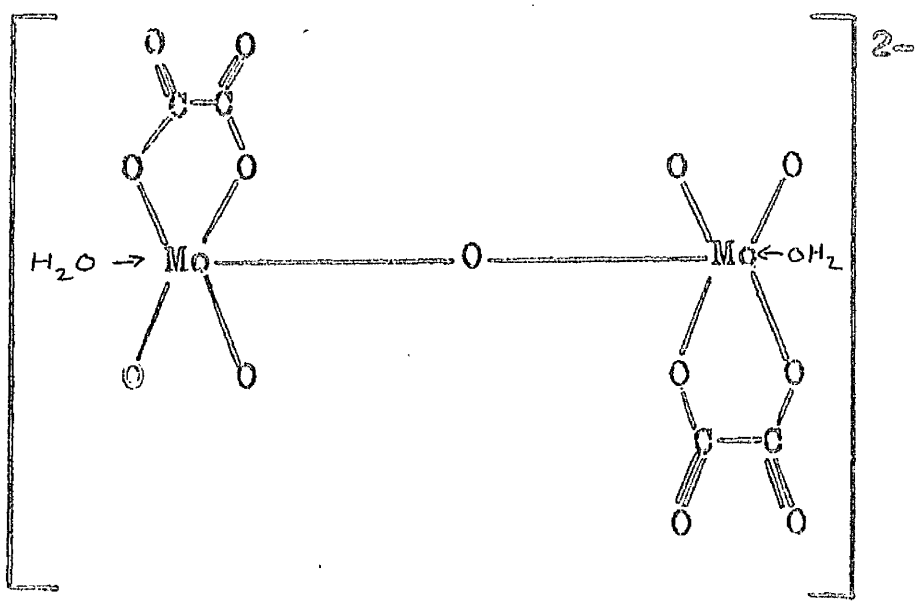
The complexes of molybdenum and tungsten appear to fall into two classes. (a) those which are formed between pH = 4.5 and 7.0 and (b) those formed between pH = 2 and 4. Those in class (a) possess a molybdenum (or tungsten): ligand ratio of 1:1 or 1:2 and those in class (b) a ratio of 2:1. Examples of class (a) are the complexes of tiron, tartaric, mandelic, oxalic, trans-aconitic and itaconic acids, and of sugars such as D(+) mannose, D(-) ribose and L(-) sorbose and examples of class (b) the complexes of D-mannitol and D-sorbitol.

Angus and Weigel[70] have suggested that the factor governing the nature of the molybdenum or tungsten species reacting, is the availability of hydroxyl groups on the ligand. They maintain that in order to keep the coordination number of the metal atom low (about six) the metallic ions polymerise to $Mo_2O_7^{2-}$ and $W_2O_7^{2-}$. However, the actual species complexing is probably more profoundly influenced by the pH of the solution than by the nature of the ligand. Accordingly, the complexed species in class (a) are more likely to be the simple MoO_4^{2-} and WO_4^{2-} ions, than the dimeric forms which tend to require lower pH values for

their formation.

Where class (b) is concerned, the metal: ligand ratio is 2:1 and here, because of the low pH of formation (pH = 2 to 4) there is the possibility that it is the dimeric species $Mo_2O_7^{2-}$ and $W_2O_7^{2-}$ which are complexed.

The only structural work carried out on these complexes of molybdate and tungstate has been upon the oxalic acid complex $K_2[Mo_2O_5(C_2O_4)_2(H_2O)_2]$ which was formerly considered to be the molybdenum (V) complex: $K_2[Mo_2O_6(C_2O_4)_2(H_2O)_2]$. Cotton [108], on the basis of X-ray studies, suggested that the molybdenum species was the centrosymmetric Mo_2O_5 anion possessing a rigorously linear and symmetrical Mo-O-Mo bridge, the coordination arrangement of the molybdenum being made up to octahedral by the oxalate ions as shown:



In all other cases, however, the complexes have proved to be too soluble in water to be isolated and accordingly it was

only by comparing the complexing ability of the various ligands with that of their derivatives that suggestions could be made concerning the coordination to molybdenum or tungsten of the various ligands.

In solution there is, as yet, no method of resolving the structures of these types of complexes. There are two distinct mechanisms which could be involved in the formation of these complexes - each of would give rise to different coordination numbers. They may be written in the following general terms:-

$$MoO_4^{2-} + (OH)_2L \longrightarrow [MoO_4(OH)_2L]^{2-}$$

or $$MoO_4 + (OH)_2L \longrightarrow MoO_2.O_2L + 2H_2O,$$

i.e. either a mechanism involving straight addition of the ligand or one involving elimination of water from the molybdate - ligand complex. From the consideration of pH changes associated with the reactions[103] and from the extreme solubility of the complexes in water it seems likely that the first of the two mechanisms would be the dominant reaction. In the subsequent discussion the addition mechanism is assumed to be operating. If, however, this is not the case the coordination numbers will be lower but the stoichiometry of the complexes will not be affected.

§6.2 Single Ligand and Hetero-Complexes Involving Hydroxy-carboxylic Acids and Dihydroxy-phenols.

(i) Hetero complexes with D(+) Tartaric Acid and Tiron:

Since the values of optical rotation of the D(+) tartrate-molybdate and tungstate solutions depend upon the concentration of the complexes, the fact that the addition of tiron did not greatly affect the variation of their optical rotations with pH (graphs 2) meant that the tiron had not complexed preferentially with the molybdate and tungstate at the expense of the D(+)$_{\gamma}$ tartaric acid. The introduction of tartaric acid into the tiron-complexes, on the other hand, had little effect upon the variation with pH of the optical density of the molybdate-tiron complex but produced a considerable decrease (to about one half of the original value) in that of the tungstate-tiron complex (graphs 1). No satisfactory explanation can be given for this but it presumably reflects a rather weaker interaction of the tartratotungstate with tiron due to the increased electron density on the tungsten as discussed below.

The Job Plots (graph 3) confirmed the stoichiometry of the complex as 1:1:1 molybdate (or tungstate): D(+) tartaric acid: tiron, i.e. the D(+) tartaric acid had replaced one of the tiron molecules in the original 1:2

molybdate (or tungstate): tiron complexes, possibly according to the equation:

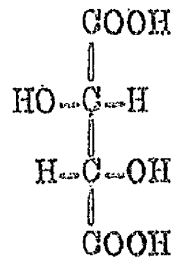
$$MoO_4[C_6H_2(OH)_2(SO_3)_2]_2^{6-} + C_4H_6O_6 \longrightarrow MoO_4[C_6H_2(OH)_2(SO_3)_2][C_4H_6O_6]^{4-} + C_6H_2(OH)_2(SO_3)_2^{2-}$$

That this hetero - complex was a stable entity could be seen from the fact that the equilibrium could not be reversed, even in the presence of a forty-fold excess of tiron, both optical density and optical rotation reaching steady values after the addition of one equivalent of tiron.

Since the optical rotation of D(+) tartaric acid alters considerably with complex formation (and only very slightly with pH) and since this difference is greater on complexing with molybdate (the stronger oxidising agent) than with tungstate the effect is apparently due, at least in part, to electron transfer from the ligand to the metal ion. The addition of another ligand e.g. oxalic acid, results in a decrease in optical rotation, presumably because the electropositive character of the metal ion has been decreased due to electron donation from this second ligand. On the other hand, addition to the tartrate-molybdate (or tungstate) of excess cation, in the form of sodium chloride, increases the optical rotation, thereby suggesting that ion-pair formation resulting in further electron withdrawal from the tartaric acid had occurred. The decrease in optical density

of the tiron complexes on the introduction of D(+) tartaric acid may similarly be ascribed to a decrease in electro-positive character of the molybdate or tungstate ion caused by the presence of the acid.

If, as seems most probable, the simple MoO_4^{2-} or WO_4^{2-} ion are the species which form complexes with tartaric acid, then, assuming that both the carboxylic acid groups and the hydroxyl groups could be involved in coordination (and models suggest that this is possible)[42] a coordination ring of

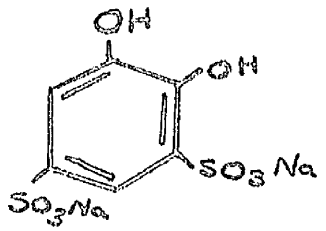


D(+) Tartaric Acid.

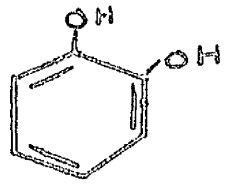
six or eight oxygens around the molybdenum (or tungsten) would be obtained. That such a scheme would be feasible is shown by the fact that other eight-coordinate compounds such as $K_4Mo(CN)_8$[104] are known.

In the case of the tiron complexes the metal ion would appear to be involved with the π bonding system of the benzene ring through oxygen bridges involving the two

hydroxyl groups. This may be deduced as follows. The introduction of substituents into the benzene ring of phenols produced a large alteration in the intensity of absorption, without there being any great change in wavelength of the absorption peak.



Tiron



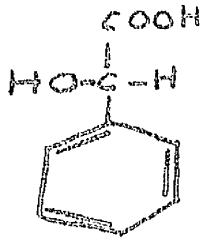
Catechol.

Since the bonding of the molybdenum or tungsten seems to take place through the two hydroxyl groups of the tiron and the two carboxyl groups and α-hydroxy groups of the D(+) tartaric acid the metal atom in these hetero complex could be up to ten coordinate.

(ii) Hetero-complexes with L(-) mandelic acid and Tiron: With L(-) mandelic acid in place of D(+) tartaric acid a similar set of results was obtained. For the tungstate hetero-complex the variation of optical rotation with pH of the mandelato complex was not affected to any great extent by the addition of tiron. Nor did the introduction of mandelic acid into the tungstate-tiron greatly affect the

variation of optical density with pH of the complex.

As indicated previously (p, 26) the intensity of absorption of the hetero-molybdate complex meant that it was not possible to follow the effect of the addition of tiron on the variation of optical rotation with pH of the mandelato-complex. However, the shape of the graph of optical density against pH for the molybdate-tiron complex did not alter on the addition of mandelic acid, thus indicating that tiron remained bonded to molybdate in the presence of mandelic acid. The maximum of the Job Plot of optical density against mole fraction of the mandelato complex (graph 3c) occurring at the molar ratio of 0.5 meant that one of the tiron molecules had been replaced by a molecule of mandelic acid to form a 1:1:1 hetero-molybdate complex. A similar result was obtained for the tungstate complex.



L(-) Mandelic Acid.

The mandelato complex, itself is a 1:2 molybdate (or tungstate): acid complex in which the two molecules of

acid probably are coordinated to the metal atom through the oxygens of the carboxylic groups and those of the α-hydroxyl groups i.e. the molybdenum(or tungsten) is eight-coordinate. Accordingly when one of the mandelic acid molecules is replaced by a molecule of tiron there is no change in the coordination number, the tiron complexes themselves being eight-coordinated.

(iii) Hetero-Complexes with Oxalic and with D(+) Tartaric Acids: It was somewhat more difficult to follow complex formation involving oxalic, trans-aconitic or itaconic acids since none of these acids are optically active, nor was there any significant alteration in their ultraviolet spectra on complex formation. However, for oxalic acid, the steady value of optical rotation reached after the addition of one equivalent of oxalic acid to D(+) tartrato-molybdate and tungstate solutions (graphs 5) suggested that 1:1:1 complexes could be formed, involving both tartaric and oxalic acids. This stoichiometry was confirmed from the results for the corrected Job Plot of optical rotation against mole fraction of the 1:1 oxalato complex (graph 3e), the possible reaction being:

$$MoO_4(C_2H_2O_4)^{2-} + C_4H_6O_6 \longrightarrow MoO_4(C_2H_2O_4)(C_4H_6O_6)^{2-}$$

Since oxalic acid is a bidentate ligand the molybdenum

(or tungsten) in the hetero complex which it forms with D(+) tartaric acid will possibly be ten-coordinate.

(IV) Single Ligand Complexes with Trans-aconitic and Itaconic Acids and the Corresponding Hetero Complex with Tiron: Conductivity measurements on the addition of oxalic acid solution to molybdate and tungstate[105] solutions showed that two different processes were operating - not only was the oxalic acid complexing with molybdate and tungstate but also it was causing these ions to polymerize, resulting in equivalence points which diverged from the theoretical values. This polymerization effect could, therefore, account for the poor agreement between theoretical and experimental equivalence points for the addition of solutions of trans-aconitic acid and itaconic acid to solutions of molybdate and tungstate.

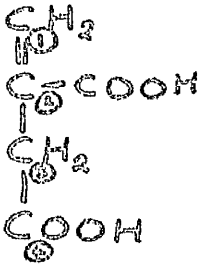
It was possible, however, to reason back to the existence of a 1:1 molybdate: acid complex from the fact that the Job Plots of optical density against mole fraction of molybdate-trans-aconitic acid and molybdate-itaconic acid-tiron solutions had their maxima of optical density at the point corresponding to the addition of one equivalent of tiron and not two, which would have been the case had there been no hetero complex formed.(graphs 8A and C). Again,

neither of the two acids affected the variation of optical density with pH for the molybdate-tiron complex (graphs 7 and 9).

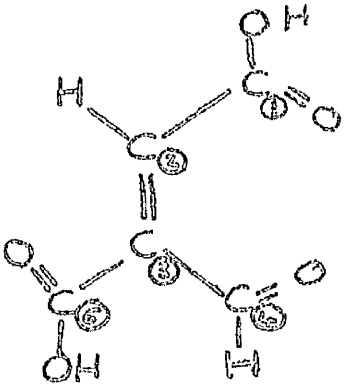
The complexing ability of the two acids proved to be rather weak since addition of tiron to the 1:1 acid: tungstate complexes resulted in displacement of the acid by the tiron to form the 1:2 tungstate: tiron complex. This process was evident from the Job Plots of optical density against mole fraction of the aconitic and itaconic acid: tungstate complexes. These showed peaks at 0.33 (graphs 8B and D), indicating the presence of only the 1:2 tungstate: tiron complex.

Baillie and Brown[42] in suggesting possible structures for the tartrato-molybdate and tungstate complexes proposed that, by analogy with the hetero-poly acids it might be desirable for the oxygen-oxygen distance in these complexes to be of the order of 3.0 A. Assuming that this suggestion is correct then examination of molecular models showed that certain of the oxygens in the two acids were this distance apart. For trans-aconitic acid the oxygens concerned would be those of the carbonyl or hydroxyl groups on C(1) and C(4), while in the case of itaconic acid the oxygens are those of the carbonyl or hydroxyl groups on C(2) and C(4). Because

only two of the oxygens in each acid are thus co-ordinated the single ligand complexes could be six coordinate and the hetero complexes with tiron eight coordinate.



Itaconic acid.



Trans-aconitic acid

§6.3. Single Ligand and Hetero-Complexes Involving Sugars and Tiron.

(i) Hetero-Complexes With D(+) Mannose and Tiron and D(-) Ribose and Tiron; Experiments With D(+) Tartaric Acid; The work of Spence and Kiang[82] concerning the variation with pH of the optical rotation of molybdate solutions containing D(+)mannose and D(-) ribose was repeated and their results confirmed. In all four cases the ratio of metal ion to sugar was found to be 1:1.

For these sugar complexes Angus and Weigel[78] suggested that the metallic ion would be in the dimeric form $Mo_2O_7^{2-}$ or $W_2O_7^{2-}$, but in view of the fact that the upper limit of

complexing is around pH = 7.5 and that optimum complexing takes place at pH = 5.5 it would appear that the simple MoO_4^{2-} or WO_4^{2-} ion is the complexing agent.

The formation of a hetero-molybdate complex involving both tiron and D(+) mannose could be confirmed by the fact that the variation of optical rotation with pH of the molybdate-D(+) mannose complex was not affected by the introduction of tiron (graphs 11), i.e. the tiron did not preferentially complex with the molybdate. Nor was the variation of optical density with pH of the tiron-molybdate complex affected by the addition of D(+) mannose or of D(-)ribose (graphs 10 and 14 respectively). This latter fact means that only one of the tiron molecules in the 1:2 molybdate-tiron complex was replaced by D(+) mannose or D(-) ribose. This stoichiometry could indeed be confirmed from the position of the maxima of the Job Plots of optical density against mole fraction of the sugar complexes, i.e. a 1:1:1 molybdate: mannose (or ribose): tiron were formed.

The optical density of the hetero-molybdate complex with D(-) ribose and tiron, however, was too intense to permit optical rotation measurements to be taken. In the case of the tungstate analogues, the tiron complexed preferentially, maxima of Job Plots of optical density against

mole fraction of sugar complexes lying at 0.33, showing that only the 1:2 tungstate complex is formed. The reason for this must lie in the fact that the hetero-molybdate complex is relatively more stable than the molybdate-tiron complex whereas the same is not true for the tungstate analogues.

Introduction of D(+) mannose and D(-) ribose into either D(+) tartrato-molybdate or tungstate solutions did not result in hetero-complex formation. The maxima at 0.5 in the Job Plots of optical rotation against mole fraction of the molybdate and tungstate-(+) mannose (or D(-) ribose) complexes merely indicated the preferential formation of the 1:1 tartrate complexes. The coincident plots showing variation of optical rotation with pH (graphs 12 and 15) suggest the same thing. That the tartaric acid had preferentially complexed with the molybdate and tungstate could also be seen from the fact that the addition of meso-tartaric acid to solutions of D(+) mannose and D(-) ribose complexes resulted in the reduction of the optical rotation of the D(+) mannose and D(-) ribose to the values they possess when uncomplexed (graphs 13 and 16). The corrected Job Plots consisted of a smooth decreasing curve for the tungstate ion, while that for the molybdate showed a slight minimum, these results indicating that no simple hetero-

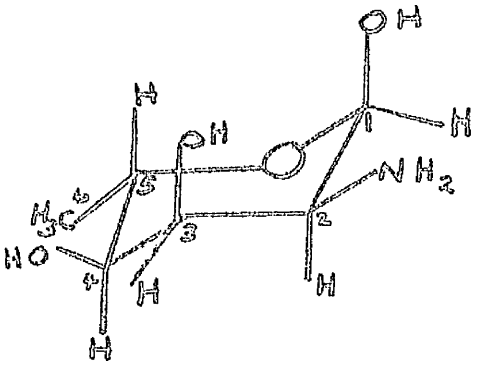
complex was being formed.

With the sugar complexes the steric effect becomes more significant and may provide the explanation as to why hetero-complexes are formed with tiron but not with D(+)tartaric acid. The hydroxyl groups in tiron are attached to adjacent carbon atoms whence it would be possible to accomodate the molecule into a metallic ion which was already coordinated to the ring structure of a sugar. In the case of tartaric acid, if both the carbonyl groups and the hydroxyl groups are involved in the bonding, the tartaric acid molecule would require to envelope the molybdate ion to some extent and this would not be possible where the molybdate ion was already coordinated to a sugar ring structure.

Where sugar complexes are concerned, it is not yet clear how many of the oxygens of the hydroxyl groups are involved in the bonding to the molybdate or tungstate ion. Spence and Kiang [83] originally suggested that three adjacent hydroxyl groups in the 1(axial), 2(equatorial), 3(axial) configuration were essential for complex formation between a sugar and molybdate or tungstate ions, the sugar functioning as a tridentate ligand.

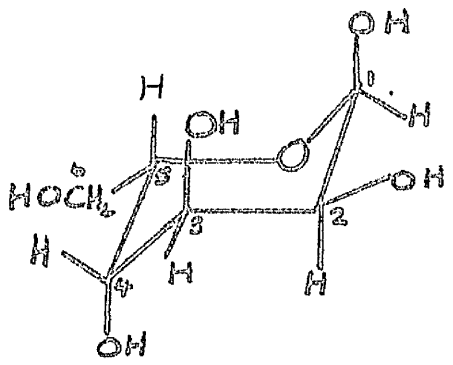
Angus, Bourne, Searle and Weigel[84] with experiments

involving an amino substituted sugar: 2- amino - 2,6 - dideoxy - D - talo - hexose:

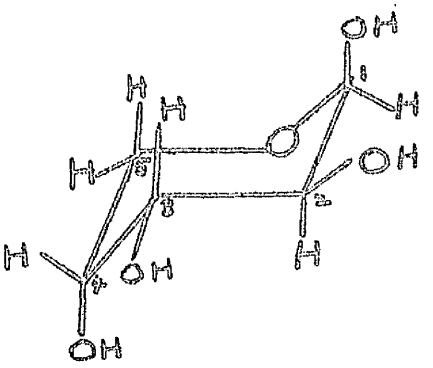


found this to be incorrect, since this sugar also complexed with molybdate and tungstate. What can be said is the following. Firstly, the optical rotation of D(+) mannose [63] changes sign from positive to negative on complex formation because of the alpha isomer (which is predominent in solution) being converted into the beta-form in order to complex with the molybdate and tungstate. This suggests that the first of the three hydroxyl groups (on carbon number 1 in this instance) must be axial and is essential to complex formation.

Secondly, since β-D(-) arabinose, which is identical to β-D(+) mannose except at c(3) where the hydroxyl group in arabinose is equatorial, does not complex it follows that the third hydroxyl group must also be axial. Thirdly from the fact that β-D(+) glucose and β-D(+) galactose

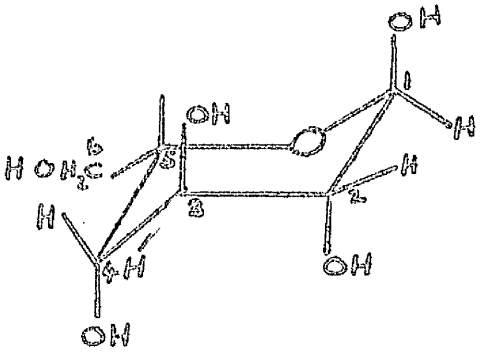


β - D(+) Mannose

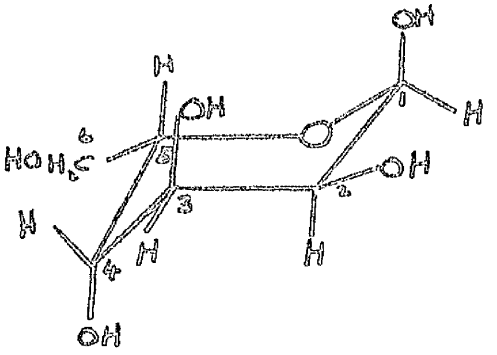


β - D(-) Arabinose.

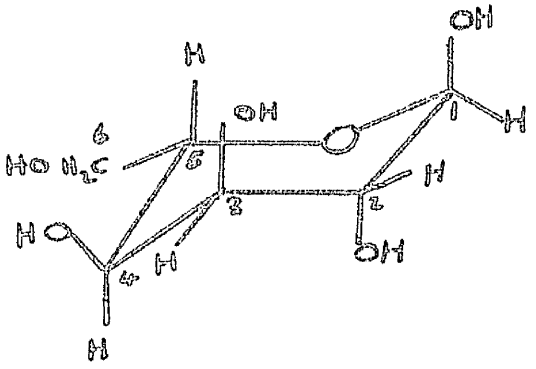
respectively have the same configuration at C(1) and C(3) as β-D(+) mannose and β-D(-) lyxose and that



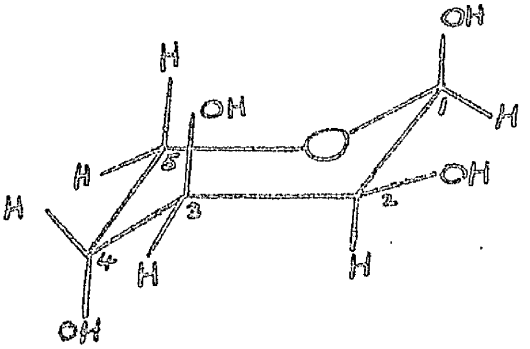
β - D(+) glucose



β- D(+) mannose.

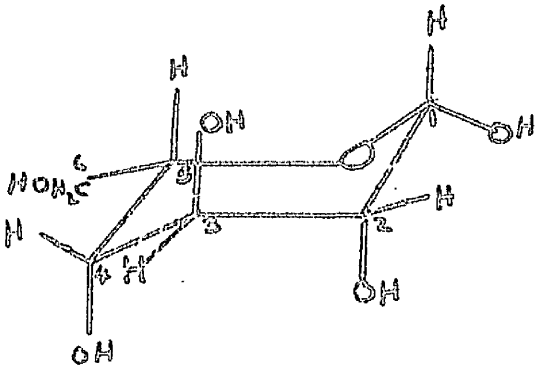


β - D(+) galactose

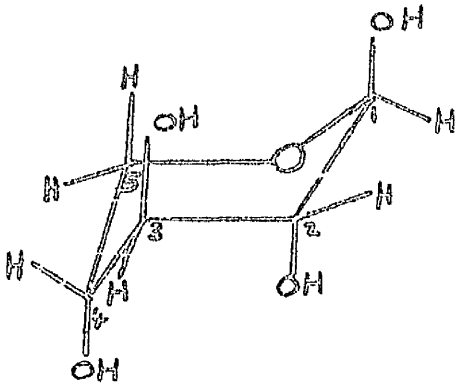


β- D(-) Lyxose.

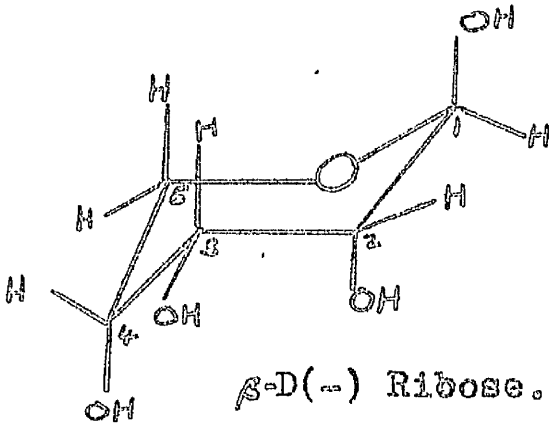
α-D(+) glucose and β-D(-) xylose have the same configuration at C(2) and C(4) as β-D(-) ribose and yet do not complex it follows that a third substituent at the intervening carbon atom is apparently necessary for complex formation to take place.



α - D(+) glucose



β -D(-) Xylose



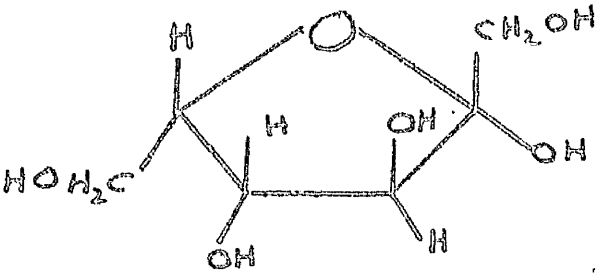
β-D(-) Ribose.

This third group need not necessarily be a hydroxyl group - it can be a primary amino group - but it must occupy an equatorial position since an axial hydroxyl group appears to be completely ineffective (α or β-D(+) glucose).

The actual function of this third hydroxyl group is still not clear. Angus and Weigel [78] suggest that it is eliminated as water to enable two molecules of sugar to complex with the dimeric species $Mo_2O_7^{2-}$, but in view of the value of pH (5.5) at which optimum complexing takes place, this mechanism is unlikely. A possible alternative explanation may be that both hydroxyl and amino substituents in the intermediate equatorial position give rise to intramolecular hydrogen bonding with the two axial hydroxyl groups, this bonding being essential to the stabilization of the complex.

(ii) Single Ligand Complexes With L(-) Sorbose and the Corresponding Hetero Complex With Tiron: There is a considerable difference between the variation of optical rotation with pH for L(-) sorbose alone and that for L(-) sorbose dissolved in sodium molybdate and tungstate. Hudson [106] showed that the species present almost exclusively in aqueous solution is the alpha-isomer: L(-) sorbose. The large decrease in the negative value of optical rotation (towards zero rotation) at pH = 5.5 will be due to the mutarotation of the sugar into the beta-form. Since, however, it is apparently the alpha-form which is required for the sugar to be able to complex this mutarotation was counter-

acted by the addition of sodium molybdate or tungstate (graph 17).



α - L(-) Sorbose.

The occurrence of the peak at 0.5 in the Job Plots of Optical rotation against mole fraction of molybdate or tungstate indicated that both molybdate and tungstate reacted with one molecule of L(-) sorbose.

Due to the difference in strengths of the single ligand complexes, hetero complex formation was obtained with molyas could be seen from the fact that there was little diff-plex, as could be seen from the fact that there was little difference between the plots of optical density against pH for the hetero complex solutions and the 1:2 molybdate: tiron complex, the introduction of L(-) sorbose into the molybdate-tiron complex only resulted in the replacement of one molecule of tiron. This 1:1:1 molybdate: L(-) sorbose: tiron stoichiometry was confirmed by the position of the maximum of the Job Plot of optical density against mole fraction of

sugar complex.

A somewhat analogous situation to that for D(+) mannose and D(-) ribose is said to exist in the case of L(-) sorbose. Bourne, Hutson and Weigel [82] suggested that the 1-, 2-, 3- hydroxy groups of L(-) sorbose are able to form a structure of the same relative spacings as those for the 1(axial), 2(equatorial), 3(axial) triol system. This suggests, however, that the ligand is tridentate whereas considerations for D(+) mannose and D(-) ribose tended to indicate that they, at any rate, are bidentate. At the moment there is no evidence to support either one or other point of view with regards to L(-) sorbose since it is not yet known whether one of the hydroxyl groups of L(-) sorbose is replaceable.

Assuming that the ligands are in reality bidentate, each of the single ligand complexes will possess a six - coordinate molybdenum while the hetero complexes, involving coordination to two oxygens on each ligand, will be eigh - coordinate.

g. 6.4 Single Ligand Complex With D-Sorbitol and Hetero-Complexes Involving Polyhydroxy Alcohols, Tiron and Tartaric Acid.

(i) Introduction: Two factors require to be considered where D- mannitol and D- sorbitol complexes are concerned. Firstly the values of optical rotation of these substances are very low, and secondly the pH at which maximum complexing is obtained is in the range of pH = 2 to 4. The consequence of the first factor was that the optical density of the hetero complexes involving both mannitol or sorbitol, and tiron could not be decreased in intensity by dilution to a sufficient extent to allow optical rotation measurements to be made. With the second factor there would be a tendency for the molybdate and tungstate to polymerise and for the complexed agent to be the dimolybdate or ditungstate ion. The results obtained were of such a nature that they could almost equally well be interpreted in support of this polymerization mechanism or in agreement with the accomodation of two discrete molybdate or tungstate ions per molecule of mannitol or sorbitol.

(ii) Single Ligand Complex With D-sorbitol: The addition of D-sorbitol to sodium molybdate (or tungstate) in the course of conductivity titrations seemed to result in complex

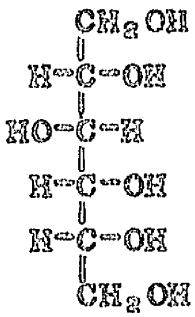
formation, either with the dimeric species ($Mo_2O_7^{2-}$ or $W_2O_7^{2-}$), or with two equivalents of the simple molybdate (or tungstate ion MoO_4^{2-} (or WO_4^{2-}) as was shown by the break in the conductivity curve (graph 6c) at the point corresponding th the metal atom: alcohol ratio = 2:1. This confirmed the findings of Angus, Bourne and Weigel[79], further support being given to this stoichiometry by the occurrence of the maximum at 0.66 in the corrected Job Plot of optical rotation against mole fraction of molybdate and tungstate. By observing the variation of optical rotation with pH (graphs 19) the range of pH for optimum complexing was found to be pH = 2.0 to 4.0.

(iii) Hetero-Complex With D-Mannitol and Tiron: With D-mannitol and tiron, evidence could only be obtained for the formation of the hetero-molybdate complex from a Job Plot of optical density against mole fraction of mannitol complex. As indicated (p.60) the concentration of the reagents were so adjusted that the fact that the maximum occurred at 0.5 meant that two molecules of tiron were accomodated in the molybdate-D- mannitol complex giving the ratio of molybdate: D-mannitol: tiron = 2:1:2. The plot of optical density against pH for this ratio of components (graph 18A) was similar to that for the tiron complexes alone, thus confirming the presence of the hetero-complex in solution.

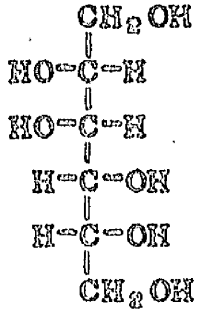
(iv) Hetero Complexes With D-Sorbitol and Tiron and D-sorbitol and D(+) Tartaric Acid. Both Job Plot and variation of optical density with pH curves (graph 18B) revealed the existence not only of the 2:1:2 molybdate: D-sorbitol: tiron complex but also of a molybdate-D-sorbitol complex containing two molecules of D(+) tartaric acid. In the case of the hetero complex with tartaric acid , Job Plots with both D(+) tartaric acid added to the D-sorbitol complex and D-sorbitol added to the meso-tartaric acid complex possessed peaks at 0.5 which, for the concentrations used, indicated the above ratio of components. Likewise the variation of optical rotation with pH for the D(+) tartrato complex was not affected by the introduction of the D-sorbitol, i.e. the two molecules of tartaric acid remained bonded to the molybdate ions (graphs 18C and D). Nor did meso-tartaric acid alter the plot for the D-sorbitol complex, thus showing that the tartaric acid did not preferentially complex with the molybdate. No tungstate analogues were formed, presumably because the tartrato-tungstate complex was relatively more stable that the tungstate-D-sorbitol complex.

As previously mentioned, the low value of pH (approximately 2.0) at which maximum complexing occurs with D-mannitol and D-sorbitol means that there is a reasonable poss-

ibility that the complexed agent is the dimeric species $Mo_2O_7^{2-}$. If it can be assumed that the molybdenum - oxygen-molybdenum distance in the $Mo_2O_7^{2-}$ ion will be of the same order as that for the solid oxalato complex examined by Cotton[102] then the molybdenum atoms in the dimolybdate ion should be approximately 3.76 A apart. If then, it is considered that the hydroxyl groups coordinated to the molybdenum atoms are those on C(1) and C(3), C(4) and C(6) of D-mannitol



D-sorbitol



D-mannitol.

and D-sorbitol measurements from molecular models indicate that the molybdenum - molybdenum distance is approximately 3.7 A. That these are the hydroxyl groups involved in the coordination tends to be confirmed by Bourne, Hutson and Weigel's[77] claim that substitution of the hydroxyls of C(2) and C(5) does not affect complex formation whereas substit-

ution of the oxygen of the hydroxyl group on C(3) completely inhibits the reaction. On the other hand, they suggest that 6-substituted sorbitol could still form a complex with a 2:1 metal: alcohol ratio and the 4 - substituted a 1:1 complex. This is, in effect, suggesting that the oxygen of the hydroxyl group on C(6) is not involved in the bonding, but this suggestion, taken in conjunction with their conclusions concerning the hydroxyl groups on the other carbon atoms being unnecessary for bonding is open to doubt since under their scheme the only hydroxyl groups essential are those on C(1), C(3) and C(4). The only mechanism which could support the use of only three hydroxyl groups in a complex possessing a metal: alcohol ratio of 2:1 would involve the two molybdenum atoms being differently coordinated - one to one hydroxyl group and the other to two. For the mannitol complex, Angus, Bourne and Weigel suggest that the bonding is from the hydroxyl groups on C(1), C(2), C(3) and C(4), but in view of the length of the metal-oxygen bridge bond this seems unlikely.

To summarise: it is suggested that coordination between molybdate and D-mannitol (and D-sorbitol) takes place via the oxygens of the hydroxyl groups on C(1) and C(3), C(4) and C(6). No definate statement can be made

regarding the nature of the molybdenum species complexed, but in view of the inter-atomic distances involved and the low pH of complex formation it may well be that the complexed agent is the dimolybdate ion $Mo_2O_7^{2-}$. With this as the metallic ion each of the molybdenum atoms in the single ligand complexes would be five coordinate, seven coordinate in the hetero-complexes with tiron and possibly nine coordinate in the hetero complex with tartaric acid.

g. 6.5. Single Ligand Complex with Hydroxylamine and the Corresponding Hetero-Complex With Tartaric Acid.

By observing the shape of the plot of optical density against pH (graph 20A) and the shape of the peak in the Job Plot of optical density against mole fraction of the sodium molybdate it was found that three days were required for solutions of the molybdate-hydroxylamine complex to come to equilibrium. The Job Plot indicated that the ratio of components was 1:1.

The considerable decrease in the variation of optical density with pH caused by the addition of D(+) tartaric acid to the molybdate-hydroxylamine complex showed that although the tartaric acid had affected the coordination of the hydroxylamine to the molybdate it did not complex preferentially with the molybdate (graphs 21). On the other hand, the

addition of hydroxylamine to the tartrate complex did not affect the nature of the curve of optical rotation against pH, i.e. the tartaric acid and hydroxylamine were coordinated simultaneously to the molybdate ion. The Job Plot showed that the ratio of components was 1:1:1 molybdate: D(+) tartaric acid: hydroxylamine.

The reason why a certain time elapsed before the solutions of both single ligand and hetero complexes reached equilibrium may be due to the formation of a polymerized species of molybdate. Until it is known what the actual complexed agent is no suggestions can be made regarding the coordination number of the molybdenum.

g. 6.5. Summary of Complexes.

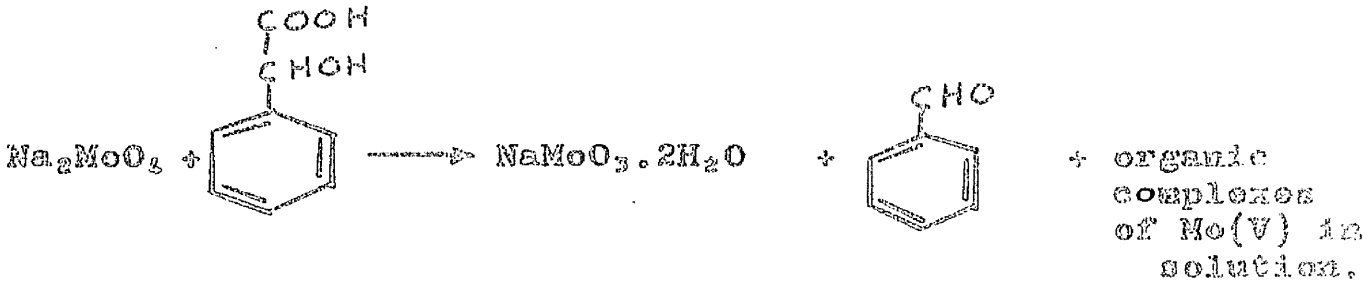
Tartaric acid forms hetero-complexes with tiron and with oxalic acid, in which there is one molecule of each of the two ligands coordinated to a single MoO_4^{2-} and WO_4^{x-} ion, the metal atom in each complex possibly being ten-coordinate. Tiron forms similar types of both hetero-molybdate and tungstate complexes (but containing eight coordinate molybdenum or tungsten) in which the second ligand is mandelic acid. Hetero-molybdate complexes alone (also eight coordinate) are formed with trans-aconitic and itaconic acids and tiron. The hydroxylamine complexes,

as indicated, may involve a polymerized species.

D(+) mannose, D(-) ribose and L(-) sorbose all form hetero-molybdate complexes with tiron in which one molecule of a sugar and one of tiron is coordinated to one simple molybdate ion (MoO_4^{2-}). Each hetero-complex is possibly eight coordinate. D-mannitol and D-sorbitol, on the other hand, form hetero-complexes with tiron, and the latter also with D(+) tartaric acid which contain one molecule of the alcohol and two molecules of the other ligand coordinated, as far as can be seen, to a single dimolybdate ion ($Mo_2O_7^{2-}$), thus giving each molybdenum atom a possible coordination of seven. Only the single ligand tungstate complexes of sugars (six-coordinate) and polyhydroxy alcohols (possibly five coordinate) are formed - the corresponding hetero-complexes are not obtained.

g.6.6. Reactions of Complexes.

Both irradiation and refluxing of solutions of molybdate complexes of tartaric acid and mandelic acid and of D(+) mannose, D(-) ribose and L(-) sorbose resulted in the reduction of the molybdenum (VI) to molybdenum (V) by the organic ligand. The reaction for the mandelic acid solutions could possibly be of the form:



As indicated, the nature of the organic complexes of molybdenum (V) present in solution could not be determined For all other ligands used, this redox mechanism either did not operate (as was the case with the complexes of citric and glycollic acids) or was only partially operative, the product being molybdenum blue - a mixture of molybdenum (VI) and molybdenum (V) (as with lactic acid, D- mannitol and D- sorbitol).

The results of the addition of various ions to these refluxed complexes varied with the nature of the ligand the general tendency being towards the stabilization of molybdenum (VI). Again, with any one ligand the effect varied with the ions used. Thus, sulphate had no effect on the refluxing of tartrato-molybdate - the red solution of molybdenum (V) still being produced. The addition of phosphate decreased the reduction to the stage of molybdenum

blue, but carbonate enabled a small degree of reduction to molybdenum (V) to take place. Nitrate and nitrite inhibited the reaction completely, traces of nitrogen dioxide (or nitric oxide) and ammonia being detected.

With the mandelato- complex the solution turned red in the presence of nitrate and nitrite, but no orange solid was deposited, while the sugar complexes were unaffected by the presence of these ions.

There are two possible explanations for the results of the introduction of nitrate and nitrite into the refluxed complexes. Firstly Coope and Thistlethwaite[10] have suggested that the nitrate ion can complex with molybdate in acid solution, whence it may be that the redox process was completely inhibited because the nitrate ion had formed a complex with molybdate which could not be reduced by the organic ligand. If this is so then this complex is not so stable, either in the presence of sugars or of mandelic acid, since in these solutions molybdenum (V) was still produced.

The alternative explanation is that molybdenum (V) is produced, but that the nitrate reacts very rapidly with it to produce molybdenum (VI) and nitrite. This nitrite, in turn, reacts with further molybdenum (V) to give nitric

oxide and molybdenum (VI).

The fact that traces of nitrogen dioxide (or nitric oxide) were formed in the solutions containing nitrate and nitrite tends to lend support to this second mechanism. Phosphate, however, forms a complex with molybdate and accordingly the first explanation is the more likely here. The carbonate likewise perhaps forms a complex which will stabilize the colourless molybdenum (VI). Sulphate, as shown by Coope and Thistlethwaite,[107] does not complex with molybdate.

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